Highly Strained Organophosphorus Compounds

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2005

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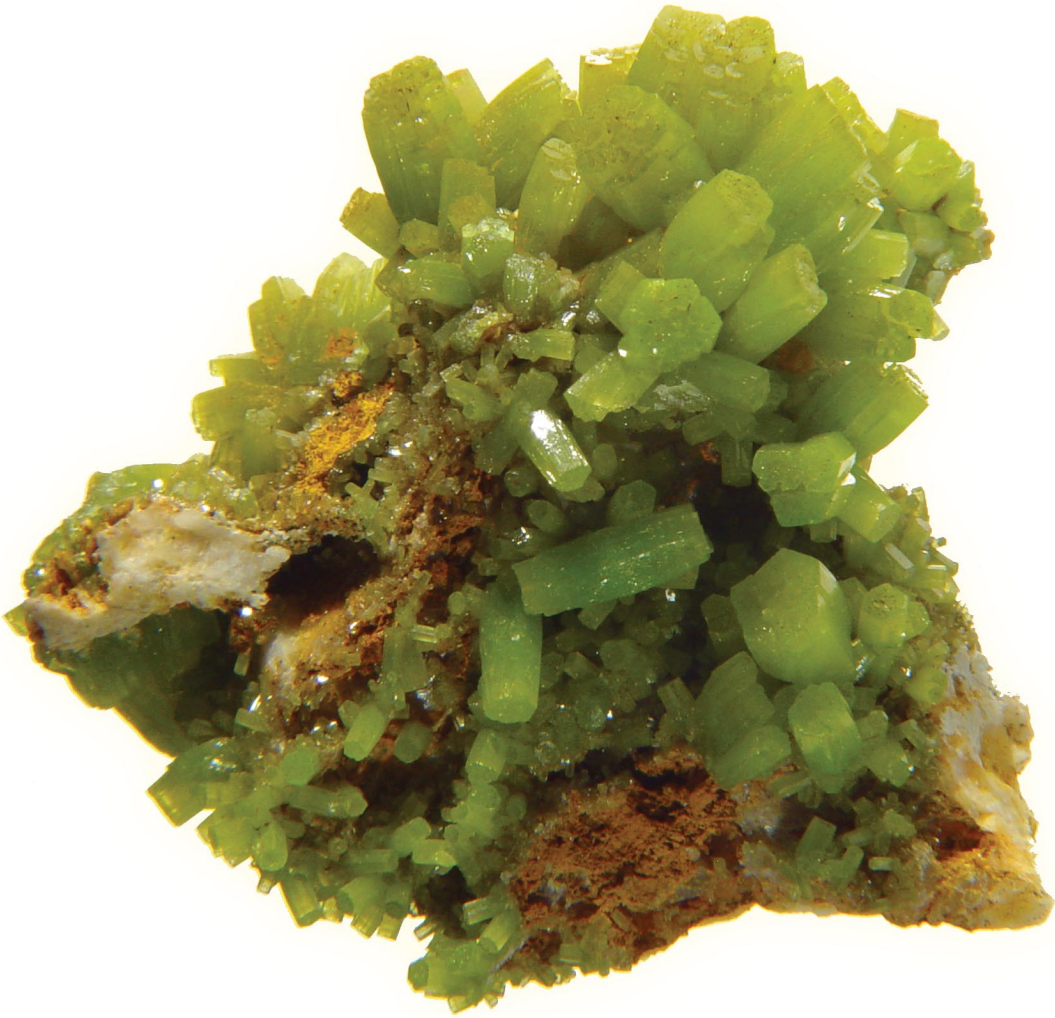

J. Chris Slootweg

The aesthetically pleasing pyromorphite, displayed on the cover of this Ph.D. thesis, was the first phosphorus-containing mineral to be discovered and reflects our quest for novel, structurally unique organophosphorus compounds. To achieve this aspiration reactive intermediate chemistry is used, supported by high-level theoretical calculations.

Highly Strained Organophosphorus Compounds

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2005

Cover illustration: Pyromorphite [$Pb_5(PO_4)_3Cl$] (Gongcheng, Guangxi, China) was the first phosphorus-containing mineral, which was discovered in 1779. In 1813, it was named after the Greek words for "fire" and "form", since after being melted a sample will begin to take on a crystalline shape during cooling.

Cover photography: Willem Dijkstra

Cover design: Corniel Nobel

ISBN: 90-901-9895-4 (978-90-90198-95-8)

VRIJE UNIVERSITEIT

Highly Strained Organophosphorus Compounds

ACADEMISCH PROEFSCHRIFT

ter verkrijging van de graad Doctor aan
de Vrije Universiteit Amsterdam,
op gezag van de rector magnificus
prof.dr. T. Sminia,
in het openbaar te verdedigen
ten overstaan van de promotiecommissie
van de faculteit der Exacte Wetenschappen
op donderdag 1 december 2005 om 10.45 uur
in het auditorium van de universiteit,
De Boelelaan 1105

door

Jacob Christiaan Slootweg

geboren te Haarlem

promotor:	prof.dr. K. Lammertsma
copromotoren:	dr. M. Schakel
	dr. A.W. Ehlers

aan mijn ouders

"It will be! the mass is working clearer!
Conviction gathers, truer, nearer!
The mystery which for Man in Nature lies
We dare to test, by knowledge led;
And what she once was wont to organize
We crystallize, instead.

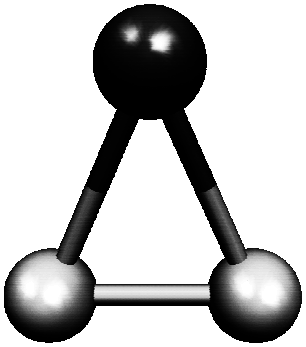
Johann Wolfgang von Goethe, "Faust, The Second Part";
Laboratory

Contents

Highly Strained Organophosphorus Compounds

1

In this introductory chapter a literature overview is given of the various reported methods for the synthesis of highly strained organophosphorus compounds. Some of these species are remarkably stable, while others function as reactive intermediates, resulting in an easy access to novel organophosphorus compounds that can serve as phosphine ligands in catalysis and as functional polymers in material science. This overview will be followed by a brief outline of the research described in this thesis.



1.1 Introduction

Phosphorus is one of the most important main-group elements and plays a crucial role in all the fields of chemistry, of which biochemistry,[1] organic synthesis,[2] coordination chemistry, homogeneous catalysis[3] and material sciences[4] are just some examples. Phosphorus heterocyclic chemistry, however, has been underdeveloped for a long time and is only recently undergoing a very rapid growth.[5] Among the phosphorus rings, the inherently strained three-membered cyclopropane and cyclopropene homologues are unique because of their profoundly different electronic and chemical properties.

1 **2** **3** **4** **5** **6**

The all-carbon cyclopropane **1** and the heterocycles oxirane **2** and azirane **3** have been studied for more than a century and are even applied as valuable starting materials for the preparation of various polymeric materials in the chemical industry. In contrast, the chemistry of the phosphorus-containing three-membered rings only started in 1963 with the discovery of the parent phosphirane **4** by Wagner.[6] The next breakthrough came 20 years later with the discovery of 1*H*-phosphirene **5**[7] and 2*H*-phosphirene **6**[8] by respectively, Mathey and Regitz. Since then, the chemistry of the three-membered phosphacycles has evolved from laboratory curiosities to indispensable tools in organophosphorus chemistry.[9] Consequently, several reviews have covered the synthesis, structure and reactivity of these intriguing species, albeit primarily focused on the ring systems containing mainly P and C.[10] In this chapter, we will give an overview of all the reported three-membered rings incorporationg one or more phosphorus atoms. Special examples of these highly interesting species will be given, like the incorporation of these ring systems into bicyclic frameworks. The applicability of strained P-rings will become evident as they give easy access to novel organophosphorus compounds and can be used as phosphine ligands in catalysis. In addition, phosphorus-containing polymers are attracting current interest, therefore these unique materials will be discussed in detail with special attention to the use of strained phosphacycles as attractive building blocks.

1.2 Three-membered Rings

The inherent strain in three-membered rings gives them their unique electronic and chemical properties due to the small angles and bent bonds.[11] Incorporation of heteroatoms and/or multiple bonds into the framework influences its strain energy and thus destabilizing factors, like angle strain and π-electron – lone pair repulsion, and stabilizing factors, like σ-aromaticity, delocalization and rehybridization can be envisioned for a variety of hetero-elements.[12] Generally, the hetero analogues of cyclopropane are less strained. However, the heteroatom-carbon bonds are much weaker than normal C–C bonds, which makes these ring systems more prone to rearrangements and are therefore even more special from a synthetic point of view.

Various synthetic routes are available for the preparation of the phosphiranes **4** and phosphirenes **5** and **6**; with the most convenient approach being the [1+2]-cycloaddition of reactive intermediates to olefins or acetylenes.[10] Consequently, the use of free or metal-complexed phosphinidenes (R–P)[13] is the most obvious and most developed route to obtain these desired phosphacycles, but the addition of carbenes, nitrenes and silylenes[14] to phospha-alkenes and –alkynes is also established. Additionally, the three-membered phosphiranes **4** have also been prepared by salt elimination reactions from P and X–Y units and cyclization of P–X–Y and X–P–Y units.[10]

To give a detailed overview, all the currently known P-containing three-membered rings are represented by their parent structures in Figure 1. These species are structurally characterized as stable, free or metal-complexed compounds, except for 3*H*-diphosphirene **10**, which has been postulated as a transient intermediate.[18]

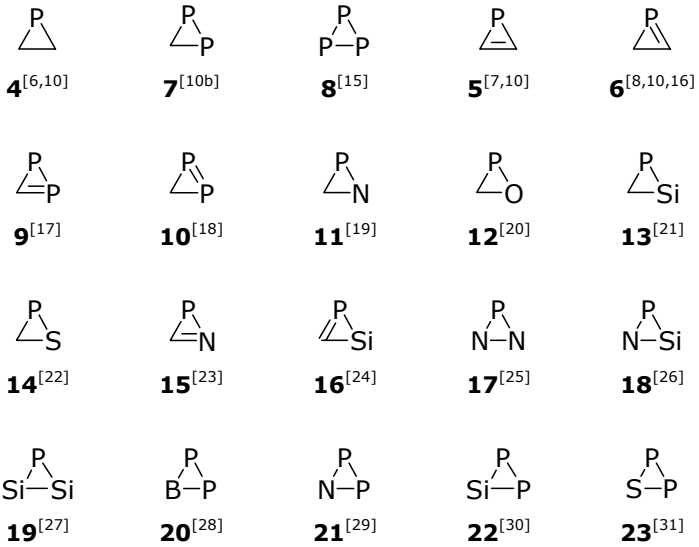
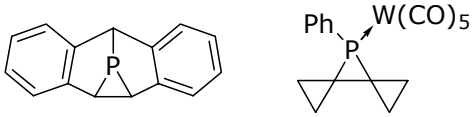


Figure 1. Parent ring structures.

Some specific examples of phosphirane **4** are the polycyclic dibenzophosphasemibullvalene **24** reported by Grützmacher[32] and the spirofused phospha[3]triangulane **25** reported by Lammertsma,[33] both synthesized by addition of low-valent phosphinidenes to the corresponding olefins.



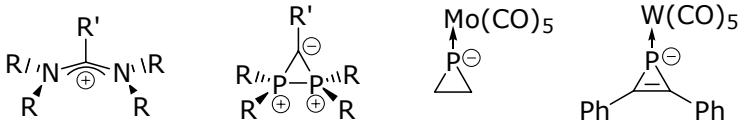
The reverse reaction is also well established and dissociation of phosphiranes and phosphirenes into alkene/alkynes and low-coordinate phosphorus units is well documented for tervalent phosphiranes,[34] phosphirane oxides,[35] phosphiranium salts,[36] and for phosphirane[37] and phosphirene[23] complexes.

Although the three-membered phosphorus-containing heterocycles have been extensively studied, their cationic counterparts have not, in contrast to the corresponding all-carbon aromatic cyclopropenium salts **26**.[38] Depicted are the two

known π-electron Hückel-type aromatic phosphirenylium cation **27**[39] and the σ-aromatic phosphirenium salt **28**,[40] which both have been structurally characterized. The only isolable diheteroatom derivatives are the recently reported diphosphirenylium **29** and diphosphirenium salt **30**.[17c,41]

26[38] **27**[39] **28**[36,40] **29**[17c,41] **30**[17c,41]

In addition, cation **32** is an exotic example, which represents the diphosphorus analogue of amidinium salt **31**. Compound **32** has been synthesized and structurally characterized as a cyclic carbanion, in sharp contrast to the open planar form, which is the most stable conformation of **31**.[42]

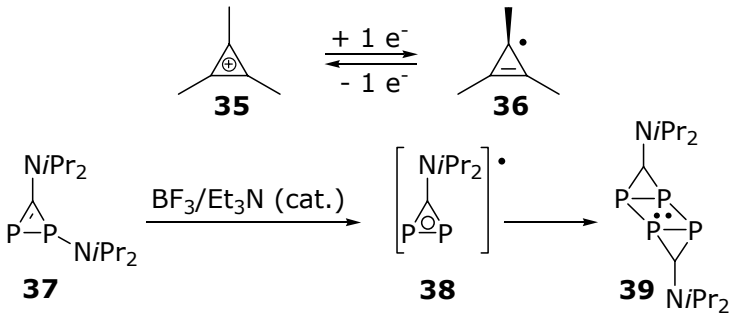


31 **32** **33** **34**

The chemistry of the anionic three-membered rings is even more limited and only complexed phosphiranide **33**[43] has been reported together with the corresponding unsaturated, anti-aromatic phosphirenide anion **34**, which can be generated in situ under phase-transfer conditions.[44] Without the stabilizing effect of the transition metal, phosphiranide and phosphirenide anions appear to be very unstable and remain, so far, elusive.

In addition, stable radical species are also not known. Whereas the all-carbon cyclopropenium salt **35** can be easily converted into the corresponding cyclopropenyl radical **36** by reduction,[45] the diphosphorus analogue **30** undergoes ring opening to yield a stable 1,3-diphosphaallyl radical.[46] However, upon cleavage of the P–N bond in 1,2-diphosphirene **37**, transient diphosphorenyl radical **38** is produced that dimerizes spontaneously yielding singlet biradical **39** (Scheme 1).

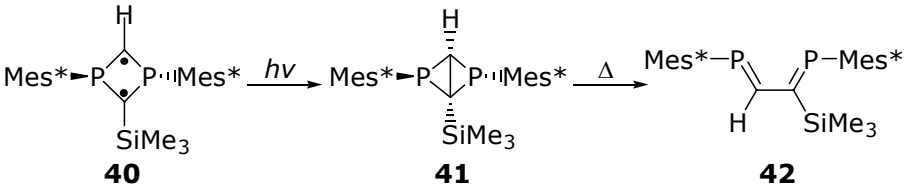
Compound **39** was described as a tetraphosphorus valence isomer of benzene with, formally, one-electron phosphorus-phosphorus bonds, which result from the π^*-π^* interaction between the two diphosphirenyl radicals.[47]



Scheme 1. Synthesis of phospha-benzene valence isomer **39**.

1.3 Bicyclo[1.1.0]butanes

Fusing three-membered rings, as in the bicyclo[1.1.0]butanes, leads to exceptional properties due to the rapid increase of ring strain. It has been shown that stretching of the central C–C σ-bond culminates in a planar singlet diradical transition structure for inversion,[48] while stretching of the peripheral bonds leads to valence isomerization.[49] Both processes are affected by the incorporation of phosphorus atoms into the bicyclic framework resulting in stable puckered bicyclic and planar diyl structures for the diphosphorus analogues. This was for the first time shown, by Niecke et al., for 2,4-diphosphabicyclo[1.1.0]butane **41**, which could be synthesized photolytically starting from crystalline 2,4-diphosphacyclobutane-1,3-diyl **40** (Scheme 2).[50] Bicyclic **41** is not stable at higher temperatures and rearranges to valence isomer butadiene **42**. Compounds **40** and **41** are the first bond-stretch isomers[51] that have been isolated and independently characterized.

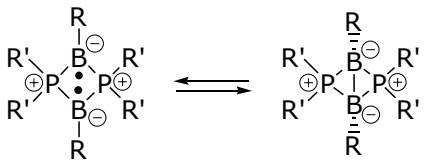


40 **41** **42**

Scheme 2. P_2-bicyclo[1.1.0]butane **41**.

Only few other phosphabicyclo[1.1.0]butanes have been reported.[52] Mathey and co-workers obtained a dihydro-diphosphabenzvalene by an *intra*molecular phosphinidene addition to the C=C bond of a 1*H*-phosphirene,[53] whereas Jones et al. used a phosphavinyl Grignard reagent to prepare an *endo*-*endo*-2,4-diphospha-bicyclo[1.1.0]butane.[54] Interestingly, in the case of the $P_2Si_2H_4$ isomers, where the carbon atoms are replaced by silicon, the diphospha-disilabicyclo[1.1.0]butanes are the most stable isomers, which can be prepared from the corresponding P,Si-butadienes.[55]

The group of Bertrand obtained both stable planar diyl and puckered forms for the isoelectronic 1,3-dibora-2,4-diphosphoniobicyclo[1.1.0]butanes **44** (Scheme 3).[56] By varying the substituents on phosphorus and boron, the first experimental evidence of bond-stretch isomerization[51] was found where, depending on the R and R' groups, derivatives of **43** and **44** with intermediate bonding patterns can be synthesized. Biradical **43** features a trans-annular bonding π-overlap, which allows for the thermal ring closure and opening processes.[57] This is in sharp contrast to Niecke's biradicaloid **40** that features a trans-annular *anti*-bonding π-overlap and therefore, the ring closure of **40** into bicyclic **41** is thermally forbidden.



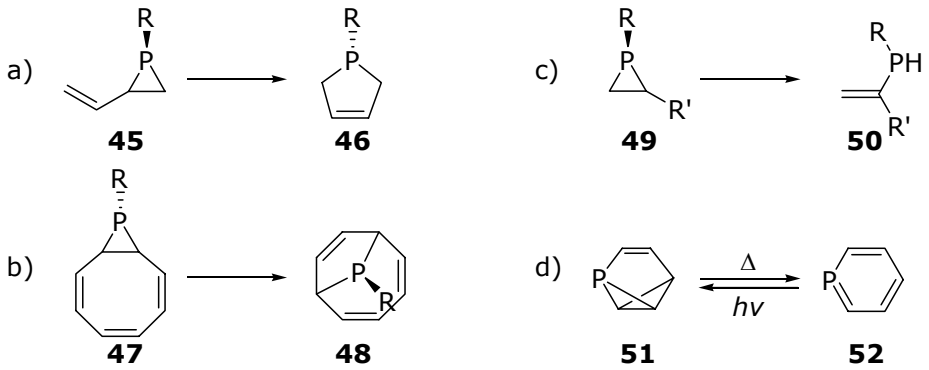
43 **44**

Scheme 3. Bond-stretch isomerization of P_2B_2-bicyclo[1.1.0]butanes **44**.

1.4 Rearrangements

The phosphorus-containing three-membered rings are more prone to rearrangements than their cyclopropane counterparts due to the weaker heteroatom–carbon bond. Consequently, a plethora of sigmatropic and electrocyclic rearrangements, involving especially phosphiranes **4**, have been observed. Because an extensive review appeared on this topic recently,[58] only the most important rearrangements, which are important for this thesis will be discussed briefly.

Among the pericyclic rearrangements of the small phosphacycles, the conversion of 2-vinylphosphirane **45** into 3-phospholene **46**, which follows a suprafacial [1,3]-sigmatropic shift, has been studied in depth (Scheme 4).[59] This hetero analogue of the well-known vinylcyclopropane-cyclopentene rearrangement[60] proceeds with diradical character for the metal-complexed phosphiranes[59g] in full analogy to the all-carbon case. In addition, the concerted antarafacial [1,5]-sigmatropic shift, that is also thermally allowed, has been established for phosphiranes like **47** (Scheme 4).[61]

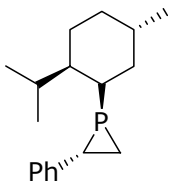


Scheme 4. Rearrangements involving phosphiranes.

Phosphiranes can also undergo a ring-chain rearrangement to vinylphosphine **50** where simultaneously a ring opening and a [1,3]-hydride shift takes place.[62] Phosphiranes incorporated into a bicyclo[1.1.0]butane framework, like **51**, generate via a thermal ring opening the more stable phosphabenzene **52**,[63] in analogy to the formation of diphosphabutadiene **42** from bicyclic **41**.

1.5 Homogenous Catalysis

Strained phosphorus heterocycles are not generally used as phosphine ligands in catalysis, but the few that are, show unprecedented behavior. Optically active phosphiranes have been obtained from their $Mo(CO)_5$-complexes by a stereoselective decomplexation reaction with $(Ph_2PCH_2)_2$ (dppe) and used as ligands for cationic rhodium(I) complexes in the catalytic hydrogenation of olefins. Significant optical yields are obtained with P-menthylphosphirane **53**, but its use was found to be limited because of ligand decomposition.[64]



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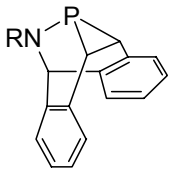

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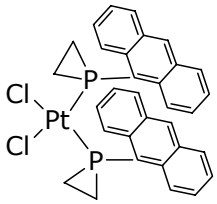


55

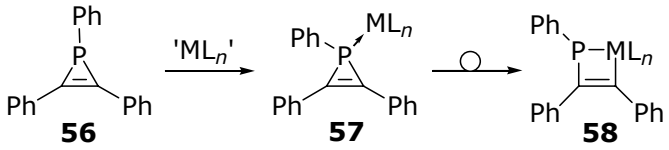
Decomposition routes for the three-membered phosphacycles are generally thermal degradation, and in addition, the monocyclic phosphiranes tend to form metallaphosphetanes as the more stable products via insertion of an electron-rich metal center into one of the P–C bonds.[65] BABAR-Phos **54**,[66] on the other hand, in which the PCC ring is incorporated into a polycyclic framework, is much more robust and allows the synthesis of fairly stable Rh(I) and Pt(0) complexes, which are active hydrosilylation[67] and recyclable hydroboration catalysts.[68] The metallaphosphetane formation with BABAR-Phos was found to be reversible and controllable by the co-ligands.

In a different vein, phosphiranes are also used as ligands for *cis*-$PtCl_2$-complexes, as in **55**, which possibly has cytotoxic properties and consequently can be used as an anti-cancer drug.[69] Interestingly, the anthracene moieties in **55** reveal π-stacking interactions in the solid state that is an important binding mode for DNA-intercalation.

The parent phosphiranes **4** are weak σ-donors due to the high s-character of the lone pair on phosphorus and as a consequence give, for example, no stable

BH_3-adducts.[70] On the other hand, phosphiranes may act as better π-acceptors as compared to other phosphines, because of the strong pyramidalization of the P-coordination sphere.[71] In contrary, the more electron-rich BABAR-Phos **54** is a relatively good electron donor, while its electron-acceptor properties are not significantly different from other phosphines.[72]

The unsaturated phosphirenes are less suited as ligands in catalysis, since complexation of 1*H*-phosphirenes, like **56**, gives phospha-metallocyclobutene **58** after rearrangement of the initially formed complex **57** (Scheme 5). Both metal-compounds have been structurally characterized.[73]



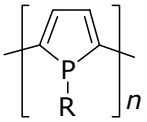
Scheme 5. Phosphirenes as ligands.

Bidentate ligands solely based on phosphiranes or phosphirenes have not been applied in catalysis yet, although these species have been reported as $W(CO)_4$-complexes, generated from transient phosphinidenes.[74] In addition, mixed phosphirane-phosphine complexes are also accessible as their $Mo(CO)_4$-adducts.[75]

1.6 Molecular Materials

Apart from catalysis, the phosphorus-containing ring systems also show promise as precursors for molecular materials. These phosphorus-containing polymers are currently attracting particular attention as catalyst support[76] and as π-conjugated materials.[77] In full analogy with the thoroughly investigated polypyrroles and polythiophenes, also phosphole-containing oligomers and polymers **59** have been prepared recently,[78] which show exciting properties, thereby opening up potential applications in optoelectronic devices such as light-emitting diodes (LEDs), polymeric sensors and TFT-based flat-panel displays. Due to the pyramidalization of the phosphorus center, orbital interaction with the conjugated π-system is reduced. As a result, the lone pair at phosphorus only functions as an n-dopant for the π-system.

Conveniently, the doping mode can be inverted easily from n- (electron donor) to p-type (electron acceptor) by simple chemical modifications such as oxidation or complexation at the phosphorus center.



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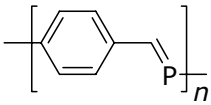

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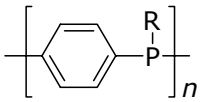
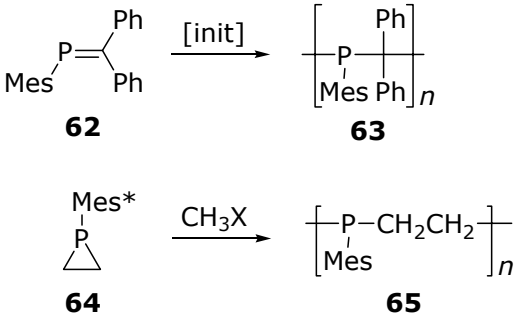


61

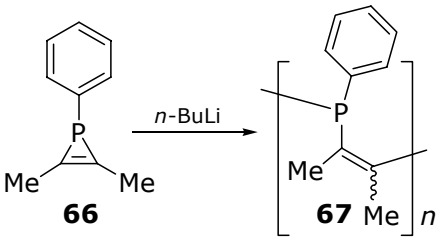
Another exciting class of luminescent macromolecules is the well-known organic poly(*p*-phenylenevinylene). The recent reported P=C double bond analogues **60**, [79] generated by condensation polymerization, also show electronic communication through the π-conjugated backbone, albeit less pronounced than their all-carbon counterparts. Related materials containing P=P bonds have also been reported, which posses interesting electronic properties, suggesting possible use as molecular switches.[80] Additionally, poly(*p*-phenylenephosphine)s **61** are the only examples where the lone pair on phosphorus is involved in extended delocalization along the polymer backbone.[81]

Saturated polymers with alternating P–C units can be obtained from phosphaalkenes by radical,[82] anionic[83] or cationic[84] polymerization (Scheme 6).[85] Recently, the remarkable ability of P=C bonds to mimic the chemistry of C=C bonds has also been applied to copolymerization of **62** with styrene and the generated macromolecules were successfully applied as catalyst support in the Pd-catalyzed Suzuki cross-coupling reaction.[86] The highly strained organophosphorus ring systems are also well suited for the production of phosphine-containing polymers by ring-opening polymerization (ROP). Surprisingly, only one report is present in the literature that treats this topic. Reaction of phosphirane **64** with a catalytic amount of cationic initiator (CH_3X; X = I, OTf) generates the desired poly(ethylenephosphine) **65** (Scheme 6).[87] Initially, a phosphiranium salt is formed, which is then attacked by the phosphorus lone pair of another trivalent phosphirane to start chain growth. In addition, ROP has also been unequivocally observed for the four-membered phosphetanes in preparing poly(propylenephosphine) materials.[88]



Scheme 6. Saturated phosphorus containing polymers.

Endocyclic double bonds, as in 1*H*-phosphirenes **5**, increase the strain of small rings significantly (SE 39 kcal·mol^{-1}) making also these species attractive monomers for applications in material science.[89] To enhance its potential, very recently, for the first time, 1*H*-phosphirenes were used to prepare polymers by anionic ROP. The novel, unencumbered 2,3-dimethyl-1-phenyl-phosphirene **66**, synthesized in an efficient one-pot reaction from commercially available starting materials,[90] polymerizes on using a catalytic amount of *n*-BuLi as initiator to give a novel class of vinylenephosphine polymers **67**, currently with molecular weights up to 63.000 (Scheme 7).[92]



Scheme 7. Synthesis of poly(vinylenephosphine) **67**.

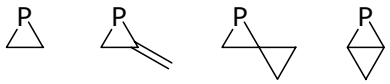
The potential of these polymers carrying phosphine units in the backbone is explored for transition metal loading, catalyst support, and conducting properties, as precursor for metal containing nanoparticles, and for cross-linking to three-dimensional arrays.

1.7 Conclusion

The highly strained organophosphorus compounds are fascinating species; some are remarkably stable, while others function as reactive intermediates generating an easy access to novel organophosphorus species that can serve as phosphine ligands in catalysis and as functional polymers in material science.

1.8 Scope and Outline of this Thesis

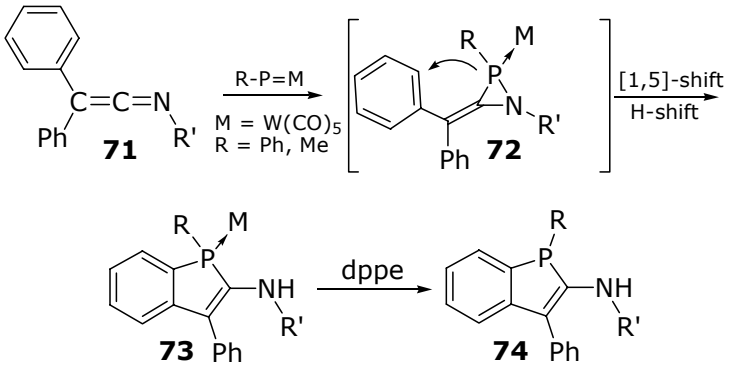
In our research on small, strained organophosphorus ring systems we became interested in the synthesis and applications of species that are even more strained than phosphirane **4** by introducing an exocyclic double bond (methylenephosphirane **68**) and by cyclopropyl spirofusion to the edge (phospha[2]triangulane **69**) and side (phosphabicyclo[1.1.0]butane **70**).



4 **68** **69** **70**

These highly strained phosphorus heterocycles are fascinating species from a fundamental point of view. Moreover, they show intriguing reactivity and remarkably facile rearrangements resulting in a large spectrum of novel organophosphorus compounds. Thus, our interest not only lies in the efficient synthesis of these highly strained phosphacycles, but also in employing them as attractive building blocks for the synthesis of phosphine ligands. To achieve this aspiration, reactive intermediate chemistry is used, supported by high-level theoretical calculations, to develop new methodologies and versatile approaches toward applicable and processable building blocks creating unprecedented entries in organophosphorus chemistry.

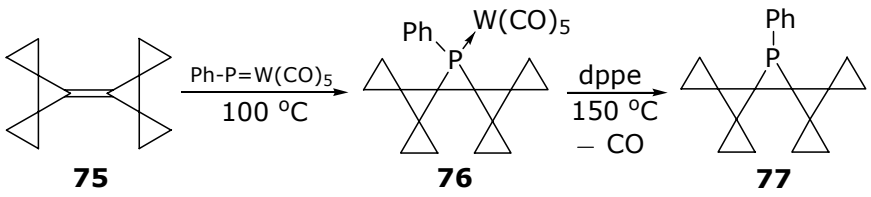
In chapter 2 we discuss the intermediacy of methylene-azaphosphiranes **72**. These species are formed from transient R-P=$W(CO)_5$ and *N*-substituted-diphenylketenimines **71**, after which rearrangement results in the novel 2-aminophosphindoles **73**, which can be demetallated to **74** (Scheme 8).



Scheme 8. Synthesis of 2-aminophosphindoles **73** and **74**.

Analysis of the reaction with DFT calculations indicates that the remarkably selective conversion of the intermediate azaphosphirane to heterocycles **73** occurs by a strain induced [1,5]-sigmatropic shift followed by a H-shift.[93]

Chapter 3 results from a collaboration with the group of Prof. Dr. A. de Meijere from the Georg-August-Universität in Göttingen (Germany) and deals with the highly strained and thermally stable, branched phospha[7]triangulane **76**, which was synthesized from the second-generation bicyclopropylidene **75** and transient, singlet phosphinidene Ph-P=$W(CO)_5$. Subsequent demetallation in refluxing xylene gave the highly stable and esthetically pleasing free phosphine **77** (Scheme 9).[94]



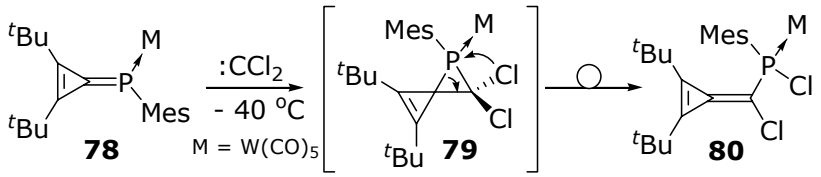
Scheme 9. Synthesis of phospha[7]triangulanes **76** and **77**.

The exceptional thermal stability of triangulanes **76** and **77**, up to 150 °C, is remarkable (SE 224 kcal·mol^{-1}), as most phosphiranes eliminate or transfer Ph-P=$W(CO)_5$ at much lower temperatures (≤ 110 °C). This behavior can be

attributed to the superior olefinic π-donor and π*-acceptor ability caused by spirocyclopropanation. A contributing factor is the release of olefin strain in **75** that amounts to 23 kcal·mol^{-1}.

Chapter 4 is an extension of chapter 3. We present the synthesis of 10 linear and branched mono- and diphospha[*n*]triangulanes by the CuCl-catalyzed phosphinidene additions to internal and external spiro-olefins. Steric factors play a role in the addition of the [PhP(Cl)W(CO)$_5$]-Cu-L (L = olefin or solvent) reagent when the substrate olefin carries a second sphere of cyclopropyl rings and causes the formation of side products.[95]

Chapter 5 deals with spirofusion of the PCC ring with cyclopropenes, which leads to unstable molecules. Dichlorocarbene addition to the exocyclic C=P bond of phosphatriafulvene **78** gives, even at low temperatures, directly triafulvene **80** with phosphaspiropentene **79** as a transient intermediate (Scheme 10).[96]

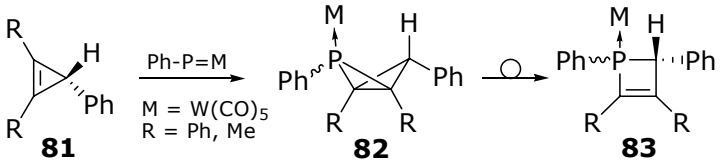


Scheme 10. Phosphaspiropentene **79** as a transient intermediate.

For the parent phosphiranes a similar rearrangement occurs at 110 °C indicating that cyclopropene substituents destabilize the PCC ring much in contrast to cyclopropanes that have a stabilizing effect.

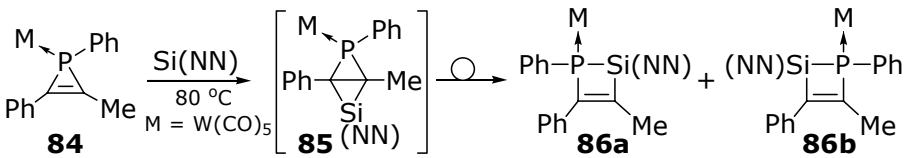
Chapter 6 deals with edge-fusion of cyclopropanes to give the much more strained bicyclo[1.1.0]butanes (SE 68 kcal·mol^{-1}), which continues to attract enormous attention. Still, the phosphorus-containing analogues remain scarce. We set out to explore the chemistry of the yet unknown 2-phosphabicyclo[1.1.0]butanes **82**, which could be synthesized by reaction of transient carbene-like Ph-P=W(CO)$_5$ with cyclopropenes **81** (Scheme 11).[97] Valence isomerization of the novel 2-phosphabicyclo[1.1.0]butanes **82**, characterized by X-ray crystallography, to the

more stable 3-phosphacyclobutenes **83** is directed by the bridge-head substituents (**82**-Ph 50 °C; **82**-Me 130 °C), which is in full analogy to the observations made for the all-carbon bicyclo[1.1.0]butanes.



Scheme 11. The first 2-phosphabicyclo[1.1.0]butanes **82**.

Chapter 7 results from a collaboration with Dr. B. Gehrhus from the University of Sussex in Brighton (England). We present herein the exploration of the yet unknown 2-phospha-4-silabicyclo[1.1.0]butanes using a different approach, that is, by reacting the thermally stable silylene Si[$(NCH_2{}^tBu)_2C_6H_4$-1,2] [≡Si(NN)] with 1*H*-phosphirene **84**. The resulting novel 2-phospha-4-silabicyclo-[1.1.0]butane **85** is a reactive intermediate that undergoes valence isomerization to the phosphasilacyclobutenes **86a** and **86b** (Scheme 12).[98]



Scheme 12. Isomerization of bicyclo[1.1.0]butane **85**.

In the final Chapter 8 we treat the experimental system of chapter 7 computationally using high-level *ab initio* calculations (QCISDT/6–311+G**//QCISD/6–31G*). 2-Phospha-4-silabicyclo[1.1.0]butane **85** isomerizes via an unprecedented symmetry allowed Woodward–Hoffmann [σ2s+σ2a] process to the thermodynamically preferred P,Si-cyclobutenes **86**. This pathway is favored over the concerted, asynchronous conrotatory ring opening leading to the open chain butadienes, which are the common decomposition products of bicyclo[1.1.0]butanes.[99]

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[90] **1-Phenyl-2,3-dimethylphosphirene**: A mixture of dichlorophenylphosphine (100 mmol, 13.7 mL) and $AlCl_3$ (100 mmol, 13.3 g) in dichloromethane (100 mL) was stirred under an inert atmosphere at room temperature until homogeneous, then cooled at –78 °C. Subsequently, 2-butyne (110 mmol, 8.6 mL) was added portionwise in 5 min and the mixture was stirred for 30 min at –78 °C; tributylphosphine (100 mmol, 24.9 mL) was then added at once into the reaction mixture at –78 °C and the mixture was stirred for 30 min at –78 °C. The solution was then warmed up to room temperature and stirred for an additional 1 h, evaporated to dryness and the residue was extracted twice with pentane (100 mL). The colorless extract was concentrated and distilled at 40 °C/10 Torr (short-path distillation) yielding 7.0 g (43 %) of a colorless, air-sensitive and thermally labile liquid. B.p. 40 °C/10 Torr; $^{31}P\{^1H\}$ NMR (101.3 MHz, C_6D_6): δ = – 182.7; $^{13}C\{^1H\}$ NMR (62.5 MHz, C_6D_6): δ = 11.2 (d, ^2J(C,P) = 9.3 Hz; *C*H_3), 118.4 (d, ^1J(C,P) = 45.6 Hz; =*C*), 128.4 (d, ^3J(C,P) = 5.2 Hz; *m*-PhP), 128.6 (d, ^4J(C,P) = 0.6 Hz; *p*-PhP), 131.1 (d, ^2J(C,P) = 20.6 Hz; *o*-PhP), 145.1 (d, ^1J(C,P) = 68.7 Hz; *ipso*-PhP); ^1H NMR (250 MHz, C_6D_6): δ = 1.96 (d, ^3J(H,P) = 4.2 Hz, 6H; C*H*$_3$), 7.09–7.16 (m, 3H; Ph*H*), 7.31–7.38 (m, 2H; *o*-Ph*H*); HR-MS

(EI, 70 eV): *m/z* (%): 162 (90) $[M]^+$, 147 (100) $[M - CH_3]^+$; calcd for $C_{10}H_{11}P$: 162.0598; found: 162.06099. **1-Phenyl-2,3-diethylphosphirene**[91] was prepared in an analogous manner and was obtained as colorless, air-sensitive and thermally labile liquid (8.6 g, 45 %). B.p. 60 °C/10 Torr; $^{31}P\{^1H\}$ NMR (101.3 MHz, C_6D_6): δ = – 186.8; $^{13}C\{^1H\}$ NMR (62.5 MHz, C_6D_6): δ = 13.0 (s; CH_3), 20.4 (d, ^2J(C,P) = 8.6 Hz; CH_2), 122.3 (d, ^1J(C,P) = 46.5 Hz; =*C*), 128.1 (d, ^3J(C,P) = 5.3 Hz; *m*-PhP), 128.4 (s; *p*-PhP), 131.1 (d, ^2J(C,P) = 20.9 Hz; *o*-PhP), 145.7 (d, ^1J(C,P) = 69.1 Hz; *ipso*-PhP); ^1H NMR (250 MHz, C_6D_6): δ = 1.05 (t, ^3J(H,H) = 7.5 Hz, 6H; CH_3), 2.45 (dq, ^3J(H,P) = 3.3 Hz, ^3J(H,H) = 7.5 Hz, 4H; CH_2), 7.11–7.16 (m, 3H; Ph*H*), 7.38–7.45 (m, 2H; *o*-Ph*H*).

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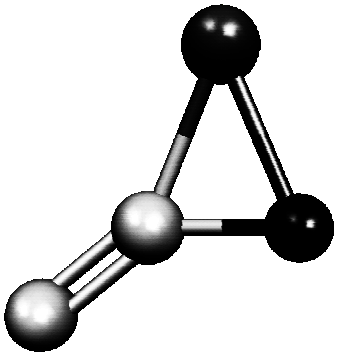
Methylene-azaphosphirane as a Reactive Intermediate

2

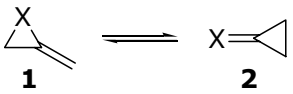
Reaction of the transient phosphinidene complexes R-P=$W(CO)_5$ with *N*-substituted-diphenylketenimines led, unexpectedly, to the novel 2-aminophosphindoles, as was confirmed by an X-ray crystal structure for one of them. Experimental evidence for a methylene-azaphosphirane intermediate (see picture) was found by using the iron-complexed phosphinidene *i*Pr_2N-P=$Fe(CO)_4$, which affords the 2-aminophosphindole together with the novel methylene-2,3-dihydro-1*H*-benzo[1,3]azaphosphole. Analysis of the reaction pathways with DFT indicates that the initially formed methylene-azaphosphirane yields both phosphorus heterocycles by way of, respectively, a [1,5]- or [1,3]-sigmatropic shift followed by a H-shift. Strain underlies both rearrangements, which causes these remarkably selective conversions that can be tuned by changing the substituents.



Published in: *Chem. Eur. J.* **2005**, *11*, 4808–4818

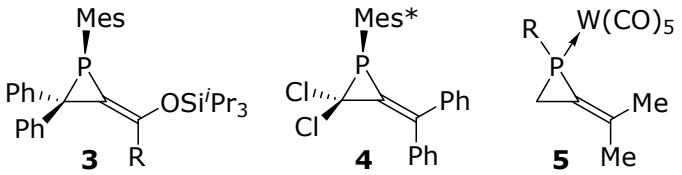
2.1 Introduction

Ring strain augmented by the presence of an exocyclic double bond makes the heteroatom analogues of methylenecyclopropane fascinating compounds.[1] Strain underlies, for example, the biradical interconversion of the valence isomers **1** and **2**, which are well-established reactive intermediates.[2] Expectantly, bulky substituents on the heteroatom, ring and/or double bond stabilize the aziridine, oxirane and thiirane derivatives, which are accessible via thermally or photochemically induced ring closures, rather then by, *e.g.*, epoxidation of or nitrene addition to allenes.[1,3]

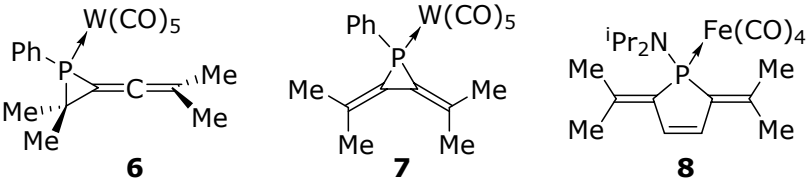


X = O, N, S, SO, SO_2

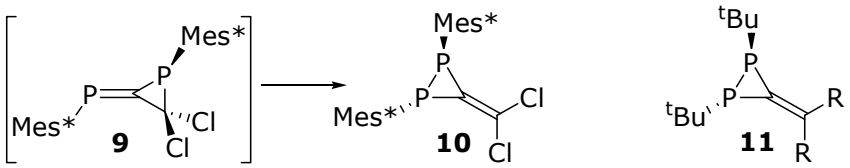
Phosphorus derivatives are similarly accessible. For instance, **3** is obtained by thermal N_2-extrusion of a diazaphosphole,[4] and compound **4** results from a dichlorocarbene addition to a 1-phosphaallene.[5] Recently, we and others have shown that very stable non-congested methylenephosphiranes, like **5**, can be obtained by the carbene-like addition of electrophilic phosphinidene complexes R-P=$W(CO)_5$[6] to allenes.[7] From cumulenes, even stable vinylidenephosphiranes **6** and phospha-[3]radialenes **7** were synthesized by this route.[8] Diallenes also give 1,2-adducts, but these convert to dimethylenephospholes **8**[9] via a [1,3]-sigmatropic shift.[10]



Mes* = 2,4,6-tri-*t*-butylphenyl



Alkylidenecyclopropanes with a second heteroatom in the ring are scarcer and the few that are known as intermediates are highly congested.[10] Of those containing two phosphorus atoms, methylenediphosphirane **10** is stable and was obtained by Yoshifuji et al. by dichlorocarbene addition to a 1,3-diphosphaallene followed by rearrangement of **9**,[5,12] while Baudler used a condensation route for the synthesis of **11**.[13] Related systems with the second heteroatom not being phosphorus are very limited.[14] Could they be accessible by 1,2-addition of a phosphinidene to heteroallenes? This is the topic of the present study in which we focus on ketenimines.



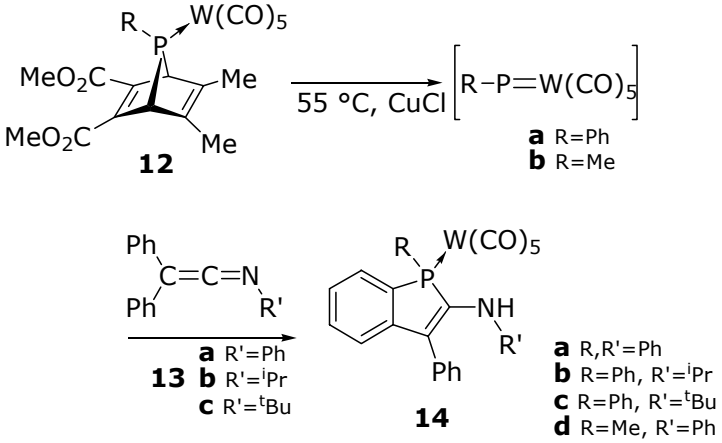
Ketenimines are readily accessible, useful building blocks in organic synthesis that have been widely applied for the synthesis of heterocycles[15] because of their ability to participate in [2+2]-cycloadditions through either the C=N or C=C bond.[16] Their reactivity toward carbenes[17] and electrophilic reagents has, however, hardly been addressed.[18]

The discussion is structured as follows. First, the experimental results are presented for the reaction of phosphinidene complexes with various ketenimines. In this section it is made plausible that alkylidene-azaphosphiranes[19] are intermediates for the formation of the observed 2-aminophosphindole products. In the next section, this premise will be supported by a survey of the potential energy surface using density functional theory.

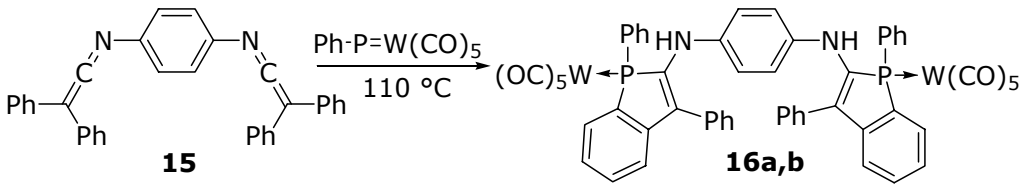
2.2 Synthesis of 2-aminophosphindoles

Reaction of the terminal phosphinidene complexes R-P=$W(CO)_5$ (R = Ph, Me), generated in situ at 55 °C by the CuCl–catalyzed decomposition[20] of its 7-phospha-norbornadiene precursor **12**,[21] with *N*-substituted-diphenylketenimines **13** resulted in the fully unexpected formation of the novel 2-aminophosphindoles **14** as sole products in moderate to excellent yields (39–91%, Scheme 1). No intermediates

could be detected by ^{31}P NMR spectroscopy. Given that in all cases one of the phenyl groups becomes P-substituted, these mild reactions are remarkably selective.



Scheme 1. Synthesis of 2-aminophosphindoles **14**.



Scheme 2. Synthesis of bis-phosphindoles **16**.

This selectivity extends to bisketenimines as reaction of **15** with two equivalents of Ph-P=W(CO)$_5$, at 110 °C, without the use of the CuCl catalyst, results in the formation of bis-phosphindoles **16** in 49% yield as a 1:1 mixture of diastereomers (Scheme 2). The structure of C_2-symmetrical complex **16a** was established unequivocally by a single-crystal X-ray structure determination (Figure 1),[22] showing the central phenyl ring with each of the *para*-amino substituents carrying a W(CO)$_5$–complexed phosphindole. The P–C bonds of **16a** are of normal lengths (P1–C1 1.842(3), P1–C8 1.826(4) and P1–C9 1.838(3) Å), whereas the C–N bonds are rather short (N1–C1 1.373(4), N1–C15 1.410(4) Å), but similar to those observed in *N*,*N*'-diphenyl-1,4-phenylenediamine.[23] The planar phosphole ring with its normal C1–P1–C8 bond angle of 89.92(14)° shows no signs of ring strain.

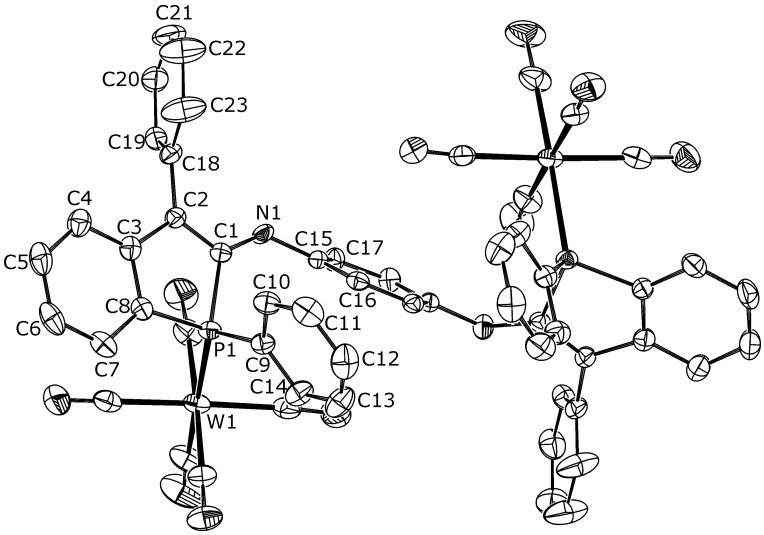
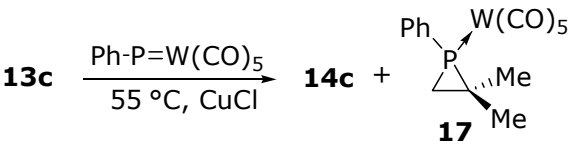


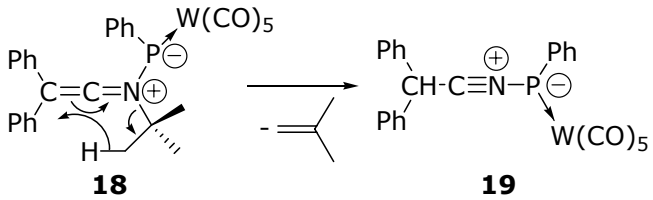
Figure 1. Displacement ellipsoid plot of **16a** with ellipsoids set at the 50% probability level. The molecule is located on an exact, crystallographic C_2 axis. Hydrogen atoms are omitted for clarity and only one orientation of the disordered phenyl group at C2 is displayed. Selected bond lengths [Å], angles and torsion angles [°]: W1–P1 2.5156(8), P1–C1 1.842(3), P1–C8 1.826(4), P1–C9 1.838(3), N1–C1 1.373(4), N1–C15 1.410(4), C1–C2 1.354(4), C2–C3 1.468(4), C3–C8 1.401(4); C1–P1–C8 89.92(14), C1–N1–C15 129.6(3); C1–C2–C3–C8 –1.0(4).

The ^{31}P NMR chemical shift of the 2-aminophosphindoles is sensitive to the P-substituent (Ph or Me); **14a-c** and **16** with a phenyl group are more deshielded (δ 12.9–17.4, ^1J(P,W) = 230–234 Hz) than **14d** with a methyl group (δ 3.0 ppm, ^1J(P,W) = 226.3 Hz).[24] The presence of the R'-NH group is evident from the sharp ^{1}H NMR resonance at δ 5.6–5.8 with a typical ^3J(H,P) coupling constant of 11–13 Hz for R' = phenyl or at δ 3.7–3.8 (^3J(H,P) = 20–23 Hz) for R' = alkyl (*i*Pr, *t*Bu).



Scheme 3.

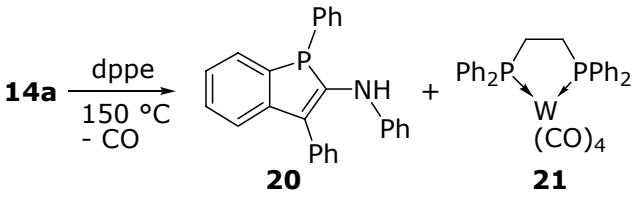
Only in one case, using *N-tert*-butyl-diphenylketenimine (**13c**), the formation of the phosphindole (**14c**, 39%) was accompanied with a byproduct (13%) that was identified as phosphirane **17** based on its ^{31}P NMR resonance at – 142.8 (Scheme 3).[25] It must originate from reaction of the phosphinidene complex with isobutene that is formed during the reaction. However, ketenimine **13c** is stable under the reaction conditions (55 °C, CuCl) in the absence of precursor **12a**; only at elevated temperatures (125 °C) **13c** does decompose into isobutene and diphenylacetonitrile.[26] A more likely source is an intermediate iminium ion as quaternary *t*-butyl-ammonium ions release isobutene even at room temperature.[27] Such a species, P,N-ylide **18**, would form on adding the phosphinidene complex to the nitrogen atom of the ketenimine. P,N-Ylides have been postulated in reactions of phosphinidenes with imines.[28] A subsequent ene-type H-shift would release isobutene and form ylide **19** that can regenerate Ph-P=$W(CO)_5$ by liberating diphenylacetonitrile[29] that was indeed detected in the reaction mixture by GC/MS (Scheme 4).



Scheme 4.

2.3 Demetallation

In view of the current increasing interest in unsaturated phosphorus ligands in homogenous catalysis,[30] we focussed our attention to the demetallation of the novel 2-aminophosphindoles. Heating $W(CO)_5$–complexed **14a**, as a test-case, with $(Ph_2PCH_2)_2$ (dppe) in refluxing xylene[31] yielded the free phosphindole **20** as the sole product together with [(dppe)$W(CO)_4$] complex **21** (Scheme 5).

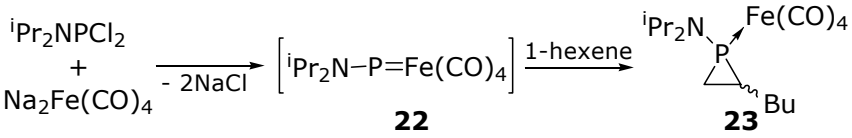


Scheme 5. Synthesis of free phosphindole **20**.

Product **20** was purified by column chromatography and could be isolated as a yellow solid in 84% yield. The removal of the [$W(CO)_5$] group is clearly reflected in the ^{31}P NMR features; its $\delta^{31}P$ at –7.4 ppm shows the expected shielding on demetallation, which is in accordance with the parent 1-phenyl-phosphindole.[32] While **14a** has sizable ^1J(C,P) couplings of 46.6 (P–C_1) and 52.8 Hz (P–C_8), the free phosphine **20** displays much smaller ^1J(C,P) couplings of 6.8 and 1.8 Hz, respectively, which resembles that for the 3,4-dimethyl-1-phenyl-1*H*-phosphole (^1J(C,P) = 43.6 Hz[33,34] versus 4.0 Hz[35]).

2.4 Identification of the intermediate

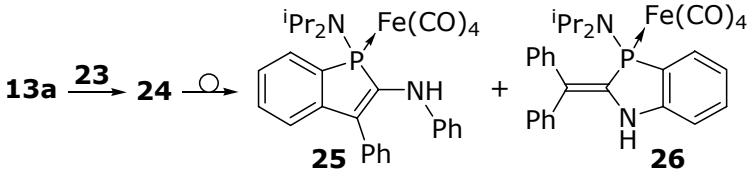
Lower reaction temperatures are needed in order to detect an intermediate in the formation of the 2-aminophosphindoles **14**, which is possible with iron complexed phosphinidene *i*Pr_2N-P=$Fe(CO)_4$ (**22**). This reagent is generated in 1-hexene by condensation of an aminodichlorophosphane with Collman's reagent, [$Na_2Fe(CO)_4$]. In this solvent it is trapped as phosphirane **23**, which is an effective reservoir of **22**, as illustrated by its quantitatively transfer to alkynes to give phosphirenes at ambient temperatures (Scheme 6).[36,37]



Scheme 6.

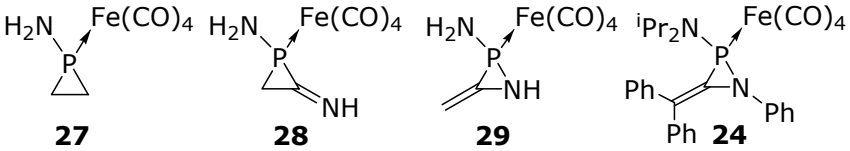
Monitoring the reaction of a 1-hexene solution of **23** (0.1M) with **13a** at room temperature with ^{31}P NMR did show the appearance of a single intermediate (37.7 ppm, 5%, 6 h), which, unfortunately, was not amenable to isolation. Performing the

reaction at the slightly elevated temperature of 40 °C gave two isolated products in a 1:1 ratio, expected 2-aminophosphindole **25** (δ^{31}P 112.3, 29%) with NMR features similar to **14** and a characteristic NH group (δ^{1}H 5.9, ^{3}J(H,P) = 4.6 Hz), and novel 1*H*-benzo[1,3]azaphosphole **26** (δ^{31}P 104.2, 29%) (Scheme 7). Interestingly, the ratio of **25** to **26** is temperature-dependent (30 °C, 2:1; 70 °C, 1:5). The assignment of **26** is based on multinuclear NMR spectra and NOE experiments showing N*H* hydrogen interactions with the *ortho*-hydrogens of the benzannelated ring and one of the phenyl groups.



Scheme 7.

To establish the nature of intermediate **24** and presuming it to originate from addition of the phosphinidene to either the C=C or C=N bond of the ketenimine, we calculated with density functional theory the ^{31}P NMR chemical shifts of model compounds **28** and **29** in comparison to parent **27**.[38]

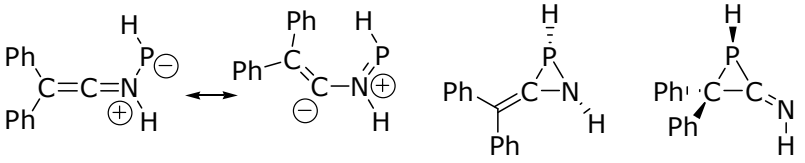


	27	**28**	**29**	**24**
^{31}P ppm	- 41.7	3.2	42.0	37.7

The calculated ^{31}P NMR chemical shift for **27** (– 41.7) is in excellent agreement with those observed experimentally (δ^{31}P – 39 to – 47) for diisopropylamino-substituted $Fe(CO)_4$–complexed phosphiranes.[37] Introducing an exocyclic imine (**28**) gives an upfield shift, but the calculated chemical shift (3.2 ppm) doesn't compare with that observed for the intermediate (δ^{31}P 37.7) in contrast to that of **29** (42.0 ppm). Therefore, we assume that the intermediate is methylene-azaphosphirane **24**.[39]

2.5 Mechanism

Two questions remain. How can a methylene-azaphosphirane rearrange to an aminophosphindole and why does an additional product result with the *i*Pr_2N-P=Fe$(CO)_4$ phosphinidene. These questions are addressed at the (U)B3LYP/ 6-31G* level of theory. To keep the calculations manageable, model structures are used without the transition metal group, without the substituent on the ketenimine nitrogen, and with the phosphorus carrying either a hydrogen or an amino group.[40]



30 **31** **32**

Three approaches of singlet phosphinidene ^{1}PH to the ketenimine are feasible, that is, to the nitrogen lone pair to give P,N-ylide **30**, addition to the C=N bond forming alkylidene-azaphosphirane **31**, and C=C bond addition resulting in phosphirane-2-ylideneamine **32**. The reaction energies leading to these three minima are 48.3, 68.4, and 66.0 kcal·mol^{-1}, respectively.[41] While P,N-ylide **30**, non-planar (ΔE = 4.9 kcal·mol^{-1}) and bent ($\angle$CCN 146.4°) due to resonance stabilization, is by far the least stable of the three it is likely the initial (kinetic) product to then convert to **31** with a barrier of 10.8 kcal·mol^{-1} (Figure 2).[42]

Starting from methylene-azaphosphirane **31**, a direct conversion into 1,7-dihydrophosphindol-2-ylideneamine **33** was found, in which the empty p orbital of the phosphorus atom attacks the π system of the nearby phenyl group, corresponding to a concerted (closed-shell) [1,5]-sigmatropic shift that requires 24.6 kcal·mol^{-1} and is exothermic by 2.8 kcal·mol^{-1} (Figure 3). The associated transition structure **TS31-33**, confirmed by an IRC calculation, has P1–C4 and P1–N1 distances of 2.579 and 2.319 Å, respectively, which are in agreement with a pericyclic Woodward–Hoffmann "allowed" concerted antarafacial [1,5]-sigmatropic shift.[43]

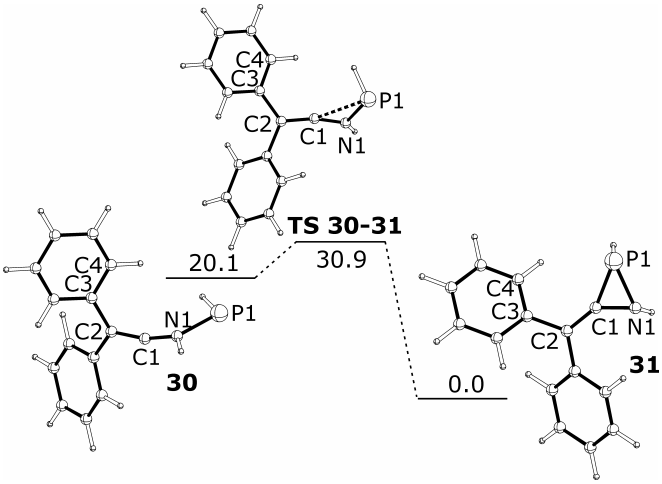


Figure 2. Relative B3LYP/6-31G* energies (in kcal·mol^{-1}) for the conversion of P,N-ylide **30** to methylene-azaphosphirane **31**. Selected bond lengths [Å] and angles [°] of **30**: P1-N1 1.795, C1-N1 1.277, C1-C2 1.321, C2-C1-N1 146.4; **TS30-31**: P1-C1 2.506, P1-N1 1.835, C1-N1 1.270, C1-C2 1.328; **31**: P1-C1 1.809, P1-N1 1.823, C1-N1 1.389, C1-C2 1.343, C1-P1-N1 45.0.

In addition, starting from phosphirane-2-ylideneamine **32**, a direct conversion into **33** with inversion of the phosphorus center was found as well, representing a concerted (closed-shell) [1,3]-sigmatropic shift that requires 20.5 kcal·mol^{-1} and is exothermic by 5.3 kcal·mol^{-1} (Figure 3). The associated transition structure **TS32-33** has P1–C2 and P1–C4 distances of 2.681 and 2.704 Å, respectively, which are in the expected bonding range for a Woodward–Hoffmann "allowed" concerted suprafacial [1,3]-sigmatropic shift.[10] Both of these rearrangements can be considered, at least formally, as an *intra*-molecular electrophilic aromatic substitution with replacement of an *ortho*-hydrogen from the phenyl group for a phosphorus obtaining Wheland intermediate **33**.[44] However, both rearrangements are unusual. While the [1,3]-sigmatropic shift of vinylphosphiranes into phospholenes is experimentally ascertained,[45,46] there is scant precedent for this type of rearrangement with aromatics.[47] In addition, the [1,5]-sigmatropic phosphirane–phospholene rearrangement has also been observed experimentally,[43] but no precedents are known for this rearrangement with aromatics. Expectedly, 2-aminophosphindole **34** is the global minimum and can be formed directly from **33** via a H-shift to nitrogen[48]

with an exothermicity of 31.4 kcal·mol^{-1}; its bond lengths are in good agreement with those experimentally ascertained for compound **16a** in the crystal.

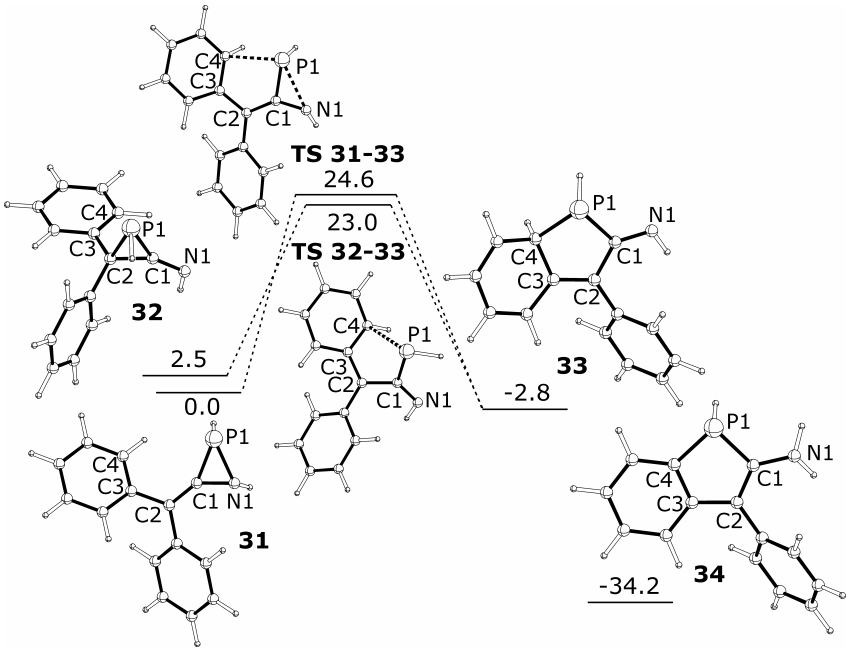
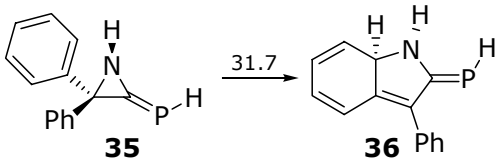


Figure 3. Relative B3LYP/6-31G* energies (in kcal·mol^{-1}) for the rearrangement of **31** and **32** into **33**. Selected bond lengths [Å] and angles [°] of **32**: P1-C1 1.836, P1-C2 1.975, C1-N1 1.261, C1-C2 1.479, C1-P1-C2 45.5; **TS31-33**: P1-C1 1.801, P1-C4 2.579, P1-N1 2.319, C1-N1 1.322, C1-C2 1.400; **TS32-33**: P1-C1 1.840, P1-C2 2.681, P1-C4 2.704, C1-N1 1.291, C1-C2 1.489; **33**: C1-N1 1.280, C1-C2 1.481, C2-C3 1.371; **34**: P1-C1 1.848, P1-C4 1.831, C1-N1 1.384, C1-C2 1.370, C2-C3 1.471, C1-P1-C4 89.3.

The special reactivity of alkylidenephosphiranes is induced by its exocyclic double bond, which increases the strain energy by 6.8 kcal·mol^{-1}, as was calculated for the parent C_3H_5P at the G3(MP2) level of theory,[8] and makes the heterocyclic ring more prone to rearrangement. Indeed, by removing the exocyclic double bond in model compound **32** the concerted [1,3]-sigmatropic shift becomes unfavorable with an endothermicity of 11.8 kcal·mol^{-1} and with a reaction barrier that increases by 18.1 to 38.6 kcal·mol^{-1} at the B3LYP/6-31G* level of theory.

To elaborate on all valence isomers of methylene-azaphosphirane **31**, we also explored the rearrangement of 2-phosphanylidene-aziridine **35** into dihydro-1*H*-indole **36**. Aziridine **35**, which is less stable than **31** by 8.3 kcal·mol^{-1} due to its more strained ring structure[49] and exocyclic C=P double bond,[7a] can indeed undergo an exothermic (ΔE = - 10.1 kcal·mol^{-1}) concerted (closed-shell) [1,3]-sigmatropic shift to **36** with inversion of the nitrogen center, albeit that the barrier of 31.7 kcal·mol^{-1} is sizeable (Scheme 8).[50]



Scheme 8.

On the basis of these DFT calculations, phosphirane-2-ylideneamine **32** cannot be excluded as intermediate in the formation of 2-aminophosphindole **34**, since it bears a comparable stability (ΔE = 2.5 kcal·mol^{-1}) to methylene-azaphosphirane **31**.[51] More importantly, both transitions, **TS31**–**33** and **TS32**–**33**, have similar energies and similar geometries at the B3LYP/6-31G* level of theory. Without bulky, stabilizing substituents, alkylidenephosphiranes are known to undergo [1,3]-shifts seemingly with diradical character[5,8,12] that raises the question whether **TS31**–**33** and **TS32**–**33** are not identical at the unrestricted level of theory. Indeed, at the UB3LYP/6-31G*, using a spin-projection method to obtain proper open-shell singlet energies,[52] the open-shell transition structure **37** ($\Delta E^{\ddagger}$ = 22.6 kcal·mol^{-1}) was found together with **38** ($\Delta E^{\ddagger}$ = 27.8 kcal·mol^{-1}, Figure 4),[53] which are the heteroatom analogues[5b] of the well-known trimethylenemethane (TMM) diradical intermediates for the interconversion of methylenecyclopropanes.[54,55] The B3LYP DFT method is capable of relatively economical direct comparisons of concerted and diradical mechanisms and is favored over the computational demanding multiconfiguration approach.[10,52]

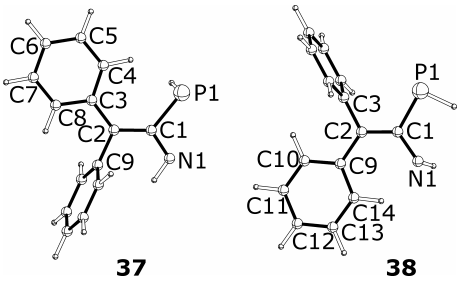
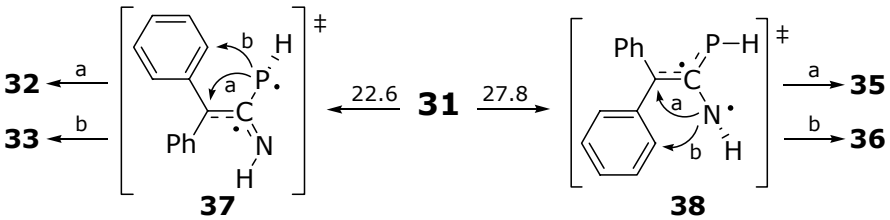


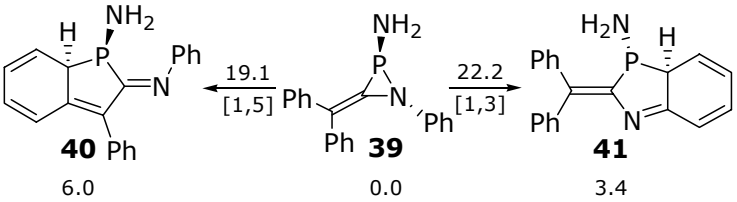
Figure 4. Open-shell transition states **37** and **38** (UB3LYP/6-31G*). Selected bond lengths [Å] and angles [°] of **37**: P1-C1 1.877, C1-N1 1.304, C1-C2 1.457, C2-C3 1.450, C2-C9 1.501, C3-C4 1.421, P1-C1-C2-C3 1.0, C1-C2-C3-C4 1.1; **38**: P1-C1 1.806, C1-N1 1.387, C1-C2 1.397, C2-C3 1.500, C2-C9 1.469, P1-C1-C2-C9 0.4, C1-C2-C9-C14 5.0.

The N/P-allyl-radical moieties of **37** and **38** are resonance stabilized through conjugation with a phenyl substituent,[56] thereby inducing radical character on the aromatic ring carbons. As a result, rearrangement to bicyclic **33** and **36** becomes possible besides formation of alkylidene-heterocyclopropanes **32** and **35**, respectively (Scheme 9). Interestingly, both diradical-like transition structures are favored over the corresponding concerted pathways (**TS31**–**33** and **TS35**–**36**), by ~2 to ~4 kcal·mol^{-1}, respectively. Therefore, the energetically most favorable process starting from azaphosphirane **31** is the diradical-like rearrangement via **37** to phosphirane **32** or phospholene **33**, with the 2-aminophosphindole **34** as the thermodynamic sink after a proton shift from **33**. The connection of open-shell transition state **38** to azaphosphirane **31** was confirmed by an IRC calculation, while tracing the IRC of **37** and **38** in all other directions was hampered by the near zero slope of the potential energy surface.



Scheme 9.

The question remains why two different products are formed on using the amino-substituted phosphinidene **22**. To address this issue we expanded the model system with a phenyl group on the nitrogen atom and an amino group on the phosphorus atom. The donating amino-substituent notably changes the characteristics of the rearrangements, favoring closed-shell pericyclic mechanisms over open-shell pathways (Figure 5).[57]



Scheme 10.

As starting point we use again the kinetic product, methylene-azaphosphirane **39**, that is formed on addition of the phosphinidene to the C=N bond of the ketenimine. From **39**, two reaction pathways are considered. Formation of 2-aminophosphindole **25** can be modeled to result from a concerted [1,5]-sigmatropic shift (**39**→**40**; see Scheme 10)[58] followed by a H-shift (**42**), which has an overall exothermicity of 22.7 kcal/mol. The first step of this process is 6.0 kcal·mol^{-1} endothermic and has a barrier (**TS39**–**40**) of 19.1 kcal·mol^{-1} that is 5.5 kcal·mol^{-1} less than for the **31**→**33** conversion. The lower barrier can be attributed to electron donation of the amino substituent, which is reflected by its planarity and the short P1–N2 bond (1.672 Å), and the stabilizing N-phenyl group. Formation of 1*H*-benzo[1,3]azaphosphole **26** can be modeled to result from a concerted [1,3]-sigmatropic shift (**39**→**41**), which is unprecedented for an azaphosphirane, followed by a H-shift (**43**) with an overall exothermicity of 23.7 kcal·mol^{-1}. The first step of this process is slightly endothermic (3.4 kcal·mol^{-1}) with a barrier (**TS39**–**41**) of 22.2 kcal·mol^{-1} that is only slightly higher than that of the [1,5]-shift, illustrating the same influence of the substituents (planar amino substituent; *d*(P1-N2) 1.672 Å). For completeness, we note that the initial "[1,5]-product" **40** can rearrange (closed-shell) to the initial "[1,3]-product" **41'**, prior to a H-shift, with a barrier of 15.2 kcal·mol^{-1} (Figure 6). The preference for the formation of **25** at 30 °C in the experiment is reflected in the lower barrier for the

conversion **39**→**40** (kinetic) compared to **39**→**41**; whereas at 70 °C, **26** is favored due to the more stable **41** (thermodynamic).

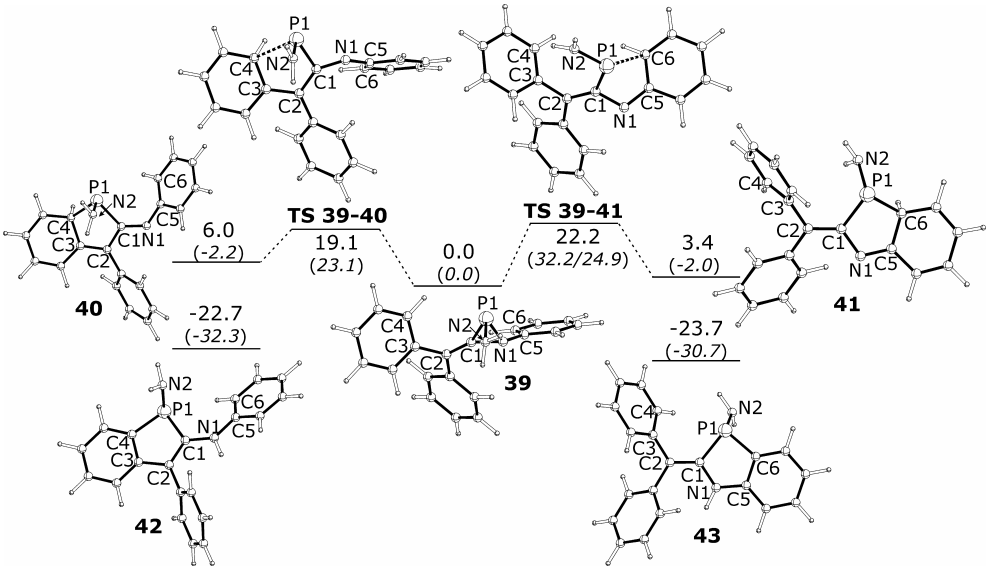


Figure 5. Relative (U)B3LYP/6-31G* energies (in kcal·mol^{-1}) for **39**–**43** (PNH_2), the relative energies (in kcal·mol^{-1}) for the unsubstituted derivatives (PH) are given in parentheses. Selected bond lengths [Å] and angles [°] of **39**: P1-C1 1.794, P1-N1 1.818, P1-N2 1.699, C1-N1 1.383, C1-C2 1.354, C1-P1-N1 45.0; **TS39-40**: P1-C1 1.839, P1-C4 2.471, P1-N2 1.672, C1-N1 1.320; **40**: P1-N2 1.723, C1-N1 1.283, C1-C2 1.475, C2-C3 1.376, C3-C4 1.519; **TS39-41**: P1-C1 1.834, P1-C6 2.663, P1-N2 1.672, C1-N1 1.394; **41**: P1-N2 1.725, C1-N1 1.396; **42**: P1-C1 1.860, P1-C4 1.833, P1-N2 1.721, C1-N1 1.380, C1-C2 1.373; **43**: P1-C1 1.892, P1-C6 1.835, P1-N2 1.729, C1-N1 1.394, C1-C2 1.366.

Next, the absence of a 1*H*-benzo[1,3]azaphosphole similar to **26** in the reaction of the phosphinidenes R-P=$W(CO)_5$ (R = Ph, Me) with ketenimines was substantiated by calculations on the model system shown in Figure 5 by using PH instead of PNH_2 derivatives. The energies of these P-unsubstituted species are again relative to **39**(PH) and are given in parentheses. The concerted [1,5]-shift for forming the 2-aminophosphindoles ($\Delta E^{\ddagger}$ = 23.1 kcal·mol^{-1}) is now favored over the [1,3]-shift that results in 1*H*-benzo[1,3]azaphospholes by way of both concerted ($\Delta E^{\ddagger}$ = 32.2 kcal·mol^{-1}) and diradical open-shell pathways ($\Delta E^{\ddagger}$ = 24.9 kcal·mol^{-1}, $\langle S^2 \rangle$ = 0.84), which concurs with the experiment. We note that the small energy difference

between the open- and closed-shell pathways is underestimated at this level of theory.[52] Expectedly, an isomerization analogous to **TS40**–**41'** does not exist for the unsubstituted derivates (PH). Complexation of the phosphorus center by $M(CO)_n$ is expected to result in a stabilization of the reagents and products, thereby further reducing the barriers for rearrangement.[10] Unfortunately, incorporation of the transition metal fragment in these reaction pathways is currently beyond our computational means.

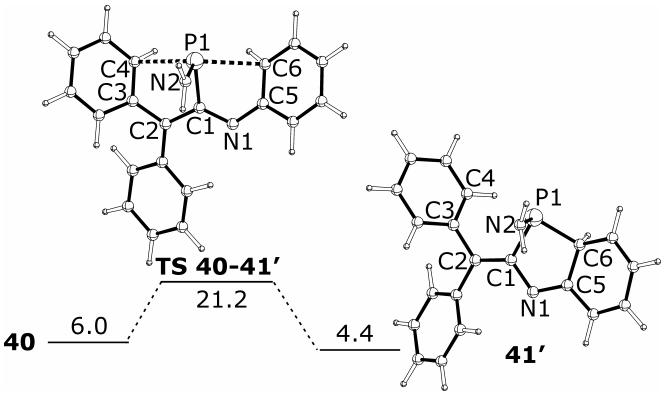


Figure 6. Relative B3LYP/6-31G* energies (in kcal·mol^{-1}) for the interconversion of **40** into **41'**. Selected bond lengths [Å] of **TS40-41'**: P1-C1 1.927, P1-C4 2.563, P1-C6 2.620, P1-N2 1.676, C1-N1 1.327, C1-C2 1.410, C2-C3 1.453, C5-N1 1.361.

2.6 Conclusion

In this paper we have described the reaction of the transient electrophilic phosphinidene complexes R-P=$W(CO)_5$ with *N*-substituted-diphenylketenimines. Each of the ketenimines gives, unexpectedly, the novel 2-aminophosphindoles as sole products, as confirmed by an X-ray crystal structure for one of them. Only *N-tert*-butyl-diphenylketenimine **13c** is not selective and decomposes partly to isobutene of which its phosphinidene addition product was isolated. No intermediates could be detected during the formation of the 2-aminophosphindoles by ^{31}P NMR spectroscopy. In contrast, experimental evidence for a methylene-azaphosphirane intermediate was found by reacting the iron-complexed phosphinidene *i*Pr_2N-P=$Fe(CO)_4$ with *N*-phenyl-diphenylketenimine that affords the 2-aminophosphindole together with the novel methylene-2,3-dihydro-1*H*-benzo[1,3]azaphosphole. Theoretical calculations at the

(U)B3LYP/6-31G* level of theory suggest that both products result from the initially formed methylene-azaphosphirane by, respectively, a [1,5]- or [1,3]-sigmatropic rearrangement followed by a H-shift. Both of these rearrangements are unusual and are facilitated by the exocyclic double bond that causes the intermediate azaphosphirane to be more strained. In agreement with the experimental observations, these remarkably selective conversions can be tuned by changing the substituents, where, an amino substituent on phosphorus stabilizes the formation of the 1*H*-benzo[1,3]azaphosphole.

2.7 Computational Section

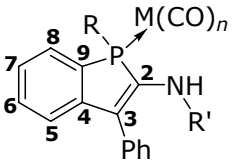
All electronic structure calculations were performed using the GAUSSIAN 98 suite of programs (G98).[59] Becke's three-parameter hybrid exchange functional[60] combined with the Lee-Yang-Parr correlation functional,[61] denoted as B3LYP, and the 6-31G* basis set was used for the density functional theory (DFT) calculations. First and second order energy derivatives were computed to confirm that minima or transition structures had been located. Intrinsic reaction coordinate driving calculations (IRC) were performed to establish connections between transition structures and minima. To extract the open-shell singlet energies from the mixture of singlet and triplet states that are obtained on calculating open-shell singlet energies with spin unrestricted DFT, we applied the spin-projection method by Houk and co-workers.[52]

The NMR calculations were performed using the Amsterdam density functional (ADF) package 2002.03.[62] In the geometry optimizations all atoms were described by a triple-ξ basis set with polarization functions, corresponding to the TZP basis set in ADF. The 1s core shell of carbon, nitrogen and oxygen and the 1s2s2p core shells of phosphorus were treated by the frozen core approximation. The metal center (Fe) was described by a triple-ξ basis set for the outer *n*s, *n*p, *n*d and (*n*+1)s orbitals, whereas the shells of lower energy were treated by the frozen core approximation. All calculations were performed at the nonlocal exchange self-consistent field (NL-SCF) level, using the local density approximation (LDA) in the Vosko–Wilk–Nusair parameterization[63] with nonlocal corrections for exchange (Becke88)[60] and correlation (Perdew86).[64] All geometries were optimized using the analytical gradient method implemented by Versluis and Ziegler,[65] including relativistic effects by the zero-order regular approximations (ZORA).[66] The ^{31}P NMR chemical shift tensors were calculated with ADF's NMR program,[67] with an all-electron basis set for the phosphorus atoms. The total isotropic shielding tensors were referenced against PMe_3, which has a value of 353.5 and an experimental chemical shift at $\delta^{31}P = -62$ with respect to 85% H_3PO_4.

2.8 Experimental Section

All experiments were performed under an atmosphere of dry nitrogen. Solvents were purified, dried, and degassed by standard techniques. NMR spectra were recorded (298K) on a Bruker Advance 250 (^{1}H, ^{13}C and ^{31}P) and MSL 400 (^{1}H, ^{13}C), internally referenced to residual solvent resonances (^{1}H: δ 7.25 ppm, ^{13}C{^{1}H}: 77.0 ppm ($CDCl_3$) and ^{1}H: δ 7.15 ppm, ^{13}C{^{1}H}: 128.0 ppm (C_6D_6) or using 85% H_3PO_4 (^{31}P) as external standard. High-resolution mass spectra (HR-MS) were recorded on a Finnigan Mat 900 and IR spectra on a Mattson-6030 Galaxy spectrophotometer. Elemental analysis was obtained from Mikroanalytisches Labor Pascher, in Remagen-Bandorf (Germany). Melting points were measured on samples in unsealed capillaries and are uncorrected.

Complexes **12a** and **12b** were prepared according to a procedure by Mathey et al.[21] *N*-phenyl-diphenylketenimine **13a**,[68] *N*-isopropyl-diphenylketenimine **13b**,[69] *N*-*tert*-butyl-diphenylketenimine **13c**,[69] *N*,*N'*-bis(diphenylethenylidene)-1,4-benzenediamine **15**[70] and complex **23**[37] were synthesized according to literature procedures. The general structure of the aminophosphindole product is shown below with numbered carbon atoms.



(1,3-Diphenyl-2-phenylamino-1*H*-phosphindole)pentacarbonyltungsten (14a): Complex **12a** (0.45 g, 0.69 mmol), *N*-phenyl-diphenylketenimine (**13a**) (0.24 g, 0.90 mmol) and CuCl (10mg, 0.1 mmol) were heated in toluene (4 mL) at 55 °C for 8 hours. Evaporation to dryness and chromatography of the residue over neutral aluminum oxide with pentane/dichloromethane (9/1) as eluent gave **14a** (0.44 g, 91%) as a pale yellow solid. Crystallization from hexane/DCM at 0 °C afforded yellow crystals. **14a**: mp 170-171 °C; ^{31}P{^{1}H} NMR (101.3 MHz, $CDCl_3$): δ = 17.4 ppm (^{1}J(P,W) = 232.7 Hz); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ = 119.4 (s; *o*-PhN), 121.8 (d, ^{3}J(C,P) = 4.9 Hz; C_5), 122.0 (s; *p*-PhN), 125.9 (d, ^{3}J(C,P) = 10.3 Hz; C_7), 128.2 (s; *p*-PhC_3), 128.6 (d, ^{2}J(C,P) = 23.9 Hz; C_3), 128.7 (s; *m*-PhN), 128.7 (d, ^{2}J(C,P) = 16.1 Hz; C_8), 129.2 (d, ^{3}J(C,P) = 10.6 Hz; *m*-PhP), 129.2 (s; *m*-PhC_3), 129.5 (s; *o*-PhC_3), 130.5 (d, ^{4}J(C,P) = 1.3 Hz; C_6), 131.4 (d, ^{4}J(C,P) = 2.4 Hz; *p*-PhP), 132.7 (d, ^{1}J(C,P) = 36.3 Hz; *ipso*-PhP), 132.8 (d, ^{2}J(C,P) = 13.5 Hz; *o*-PhP), 133.8 (d, ^{3}J(C,P) = 7.5 Hz; *ipso*-PhC_3), 138.1 (d, ^{1}J(C,P) = 52.8 Hz; C_9), 141.3 (d, ^{3}J(C,P) = 1.5 Hz; *ipso*-PhN), 143.7 (d, ^{2}J(C,P) = 8.7 Hz; C_4), 145.3 (d, ^{1}J(C,P) = 46.6 Hz; C_2), 195.9 (d, ^{2}J(C,P) = 6.7 Hz, ^{1}J(C,W) = 125.6 Hz; *cis*-CO), 197.9 ppm (d, ^{2}J(C,P) = 21.8 Hz; *trans*-CO); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 5.87 (d, ^{3}J(H,P) = 12.1 Hz, 1H; N*H*), 6.37–6.40 (m, 2H; *o*-Ph*H*N), 6.73–6.77 (m, 1H; *p*-Ph*H*N), 6.83–6.88 (m, 2H; *m*-Ph*H*N), 7.21–

7.27 (m, 2H; C_5H, C_7H), 7.31–7.48 (m, 10H; Ph*H*), 7.52–7.58 ppm (m, 2H; *o*-Ph*H*P); IR (KBr): ν = 1913, 1929 (s/br, C=O_{eq}), 2072 (m, C=O_{ax}); HR-MS (EI, 70 eV): *m/z* (%): 701 (10) $[M]^+$, 617 (26) $[M - 3CO]^+$, 561 (32) $[M - 5CO]^+$, 377 (100) $[M - W(CO)_5]^+$; calcd for $C_{31}H_{20}O_5NP^{184}W$: 701.05890; found: 701.060227; elemental analysis: calcd (%): C 53.09, H 2.87; found: C 53.15, H 2.93.

(1,3-Diphenyl-2-isopropylamino-1*H*-phosphindole)pentacarbonyltungsten (14b): Complex **12a** (0.26 g, 0.39 mmol), *N*-isopropyl-diphenylketenimine (**13b**) (0.12 g, 0.51 mmol) and CuCl (10 mg, 0.1 mmol) were heated in toluene (2.5 mL) at 55 °C for 11 hours. Evaporation to dryness and chromatography of the residue over neutral aluminum oxide with pentane/dichloromethane (9/1) as eluent gave **14b** (0.12 g, 46 %) as a pale yellow solid. Crystallization from pentane at 0 °C afforded yellow crystals. **14b**: mp 127-128 °C; $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$): δ = 12.9 ppm (^1J(P,W) = 230.4 Hz); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 23.4 (s; CH_3), 23.9 (s; CH_3), 48.6 (d, ^3J(C,P) = 5.0 Hz; $CH(CH_3)_2$), 118.5 (d, ^2J(C,P) = 15.2 Hz; C_3), 120.1 (d, ^3J(C,P) = 5.2 Hz; C_5), 123.8 (d, ^3J(C,P) = 10.7 Hz; C_7), 127.7 (s; *p*-PhC_3), 128.6 (d, ^2J(C,P) = 14.9 Hz; C_8), 129.1 (d, ^3J(C,P) = 10.4 Hz; *m*-PhP), 129.3 (s; *m*-PhC_3), 129.8 (s; *o*-PhC_3), 130.6 (d, ^4J(C,P) = 1.2 Hz; C_6), 130.8 (d, ^1J(C,P) = 36.0 Hz; *ipso*-PhP), 131.4 (d, ^4J(C,P) = 2.4 Hz; *p*-PhP), 133.1 (d, ^2J(C,P) = 13.6 Hz; *o*-PhP), 134.6 (d, ^3J(C,P) = 7.5 Hz; *ipso*-PhC_3), 136.8 (d, ^1J(C,P) = 54.4 Hz; C_9), 146.1 (d, ^2J(C,P) = 9.4 Hz; C_4), 151.6 (d, ^1J(C,P) = 51.3 Hz; C_2), 196.2 (d, ^2J(C,P) = 6.7 Hz, ^1J(C,W) = 125.6 Hz; *cis*-CO), 198.1 ppm (d, ^2J(C,P) = 21.3 Hz; *trans*-CO); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.46 (d, ^3J(H,H) = 6.3 Hz, 3H; CH_3), 0.99 (d, ^3J(H,H) = 6.3 Hz, 3H; CH_3), 3.29–3.39 (m, 1H; $CH(CH_3)_2$), 3.78 (dd, ^3J(H,H) = 10.5 Hz, ^3J(H,P) = 19.9 Hz, 1H; N*H*), 6.98–7.01 (m, 1H; C_5H), 7.06–7.12 (m, 1H; C_7H), 7.23–7.28 (m, 1H; C_6H), 7.30–7.35 (m, 1H; C_8H), 7.37–7.48 (m, 6H; *m*-Ph*H*P, *p*-Ph*H*P, *m*-Ph*H*C_3, *p*-Ph*H*C_3), 7.49–7.54 (m, 2H; *o*-Ph*H*C_3), 7.61–7.67 ppm (m, 2H; *o*-Ph*H*P); IR (KBr): ν = 1915, 1929 (s/br, C=O_{eq}), 1987 (m, C=O_{eq}), 2072 (m, C=O_{ax}); HR-MS (EI, 70 eV): *m/z* (%): 667 (24) $[M]^+$, 611 (40) $[M - 2CO]^+$, 527 (58) $[M - 5CO]^+$, 343 (100) $[M - W(CO)_5]^+$; Calcd for $C_{28}H_{22}NO_5P^{184}W$: 667.07458; Found: 667.07747.

(1,3-Diphenyl-2-*tert*-butylamino-1*H*-phosphindole)pentacarbonyltungsten (14c): Complex **12a** (84.7 mg, 129.4 µmol), *N-tert*-butyl-diphenylketenimine (**13c**) (35.5 mg, 142.4 µmol) and 1 mg CuCl (10 µmol) were heated in toluene (0.7 mL) at 55 °C for 7 hours generating 39% of **14c** and 19% of **17**[25] (^{31}P NMR yields). Evaporation to dryness and chromatography of the residue over neutral aluminum oxide with pentane/dichloromethane (19/1) as eluent gave **14c** (34.0 mg, 39 %) as a pale yellow solid and **17**[25] (8.3 mg, 13 %) as a colorless solid. Crystallization of **14c** from pentane/DCM at –20 °C afforded yellow crystals. GC-MS analysis of the reaction mixture showed the presence of diphenylacetonitrile. **14c**: mp 164 °C; $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$): δ = 19.0 ppm (^1J(P,W) = 234.0 Hz); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 30.4 (s; $C(CH_3)_3$), 53.6 (s; $C(CH_3)_3$), 121.5 (d, ^3J(C,P) = 4.8 Hz; C_5), 125.6 (d, ^3J(C,P) = 9.9

Hz; C_7), 128.1 (s; *p*-PhC_3), 128.2 (d, ^2J(C,P) = 13.2 Hz; C_8), 128.9 (d, ^3J(C,P) = 10.4 Hz; *m*-PhP), 129.3 (s; *m*-PhC_3), 130.1 (s; *o*-PhC_3), 130.2 (d, ^4J(C,P) = 1.3 Hz; C_6), 130.3 (d, ^2J(C,P) = 19 Hz; C_3), 131.1 (d, ^1J(C,P) = 35.3 Hz; *ipso*-PhP), 131.4 (d, ^4J(C,P) = 2.4 Hz; *p*-PhP), 133.5 (d, ^2J(C,P) = 13.0 Hz; *o*-PhP), 135.0 (d, ^3J(C,P) = 7.3 Hz; *ipso*-PhC_3), 140.2 (d, ^1J(C,P) = 53.1 Hz; C_9), 143.9 (d, ^2J(C,P) = 9.3 Hz; C_4), 150.9 (d, ^1J(C,P) = 47.2 Hz; C_2), 196.6 (d, ^2J(C,P) = 6.6 Hz, ^1J(C,W) = 125.9 Hz; *cis*-CO), 198.3 ppm (d, ^2J(C,P) = 21.9 Hz; *trans*-CO); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.87 (s, 9H; C*H*$_3$), 3.71 (d, ^3J(H,P) = 22.5 Hz, 1H; N*H*), 6.93–6.96 (m, 1H; C_5H), 7.14–7.18 (m, 1H; C_7H), 7.22–7.30 (m, 2H; C_6H, C_8H), 7.35–7.40 (m, 2H; *o*-Ph*H*C_3), 7.40–7.50 (m, 4H; *m*-Ph*H*P, *p*-Ph*H*P, *p*-Ph*H*C_3), 7.52–7.56 (m, 2H; *m*-Ph*H*C_3), 7.59–7.66 ppm (m, 2H; *o*-Ph*H*P); IR (KBr): ν = 1942 (s/br, C=O_{eq}), 1985 (m, C=O_{eq}), 2072 (m, C=O_{ax}); HR-MS (EI, 70 eV): *m/z* (%): 681 (15) [*M*]$^+$, 625 (15) [*M* – 2CO]$^+$, 597 (1) [*M* – 3CO]$^+$, 569 (4) [*M* – 4CO]$^+$, 541 (19) [*M* – 5CO]$^+$, 483 (25) [*M* – 5CO – *t*Bu]$^+$, 357 (100) [*M* – W(CO)$_5$]$^+$; calcd for $C_{29}H_{24}NO_5P^{184}W$: 681.08790; found: 681.09021; elemental analysis: calcd (%): C 51.12, H 3.55; found: C 51.10, H 3.57.

(1-Methyl-2-phenylamino-3-phenyl-1*H*-phosphindole)pentacarbonyltungsten (14d): Complex **12b** (0.29 g, 0.49 mmol) and *N*-phenyl-diphenylketenimine (**13a**) (0.20 g, 0.74 mmol) were heated in refluxing toluene (4 mL) for 11.5 hours. Evaporation to dryness and chromatography of the residue over neutral aluminum oxide with pentane/dichloromethane (9/1) as eluent gave **14d** (0.17 g, 54%) as a pale yellow solid. Crystallization from hexane/DCM at 0 °C afforded yellow crystals. **14d**: mp 193 °C; ^{31}P{^{1}H} NMR (101.3 MHz, $CDCl_3$): δ = 3.0 ppm (^1J(P,W) = 226.3 Hz); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ = 22.0 (d, ^1J(C,P) = 22.5 Hz; C*H*$_3$), 119.7 (s; *o*-PhN), 122.3 (d, ^3J(C,P) = 4.9 Hz; C_5), 122.7 (s; *p*-PhN), 126.1 (d, ^3J(C,P) = 10.0 Hz; C_7), 127.8 (d, ^2J(C,P) = 13.4 Hz; C_8), 128.3 (s; *p*-PhC_3), 129.1 (s; *m*-PhN, *m*-PhC_3), 129.3 (s; *o*-PhC_3), 130.5 (d, ^4J(C,P) = 1.5 Hz; C_6), 131.5 (d, ^2J(C,P) = 18.3 Hz; C_3), 133.7 (d, ^3J(C,P) = 7.0 Hz; *ipso*-PhC_3), 137.1 (d, ^1J(C,P) = 50.6 Hz; C_9), 142.3 (d, ^3J(C,P) = 1.2 Hz; *ipso*-PhN), 143.2 (d, ^2J(C,P) = 8.9 Hz; C_4), 144.0 (d, ^1J(C,P) = 47.1 Hz; C_2), 196.1 (d, ^2J(C,P) = 6.8 Hz, ^1J(C,W) = 125.4 Hz; *cis*-CO), 198.7 ppm (d, ^2J(C,P) = 20.6 Hz; *trans*-CO); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.07 (d, ^2J(H,P) = 8.0 Hz, 3H; C*H*$_3$), 5.75 (d, ^3J(H,P) = 11.4 Hz, 1H; N*H*), 6.86–6.89 (m, 2H; *o*-Ph*H*N), 6.95–6.99 (m, 1H; *p*-Ph*H*N), 7.19–7.27 (m, 3H; *m*-Ph*H*N, C_5H), 7.31–7.47 (m, 7H; C_6H, C_7H, Ph*H*C_2), 7.57–7.62 ppm (m, 1H; C_8H); HR-MS (EI, 70 eV): *m/z* (%): 639 (18) [*M*]$^+$, 555 (43) [*M* – 3CO]$^+$, 483 (35) [*M* – 5CO – Me]$^+$, 315 (100) [*M* – W(CO)$_5$]$^+$; calcd for $C_{26}H_{18}O_5NP^{184}W$: 639.04327; found: 639.040753; IR (KBr): ν = 1921, 1942 (s/br, C=O_{eq}), 1977 (m, C=O_{eq}), 2070 (m, C=O_{ax}).

(*N*,*N'*-Bis-1,3-diphenyl-1*H*-phosphindol-2-yl-1,4-phenylenediamine)pentacarbonyltungsten (16): Complex **12a** (0.66 g, 1.01 mmol) and *N*,*N'*-bis(diphenylethenylidene)-1,4-phenylenediamine (**15**) (0.21 g, 0.46 mmol) were heated in refluxing toluene (8 mL) for 14 hours. Complex **16b** precipitated as a yellow solid (0.13 g, 21%). The extract was evaporated to

dryness and the residue was chromatographed over neutral aluminum oxide with pentane/dichloromethane (4/1) as eluent to give complex **16a** (0.17 g, 28 %) as a pale yellow solid. Crystallization from hexane/DCM at 0 °C afforded yellow crystals of **16a**. **16a** (*R*, *R*) and (*S*, *S*): mp ≥ 237 °C (decomp.); $^{31}P\{^{1}H\}$ NMR (101.3 MHz, $CDCl_3$): δ = 16.5 ppm (^{1}J(P,W) = 232.8 Hz); $^{13}C\{^{1}H\}$ NMR (62.9 MHz, $CDCl_3$): δ = 120.3 (s; *o*-PhN), 121.5 (d, ^{3}J(C,P) = 4.9 Hz; C_5), 125.7 (d, ^{3}J(C,P) = 10.3 Hz; C_7), 127.6 (d, ^{2}J(C,P) = 16.3 Hz; C_3), 128.2 (s; *p*-PhC_3), 128.7 (d, ^{2}J(C,P) = 14.0 Hz; C_8), 129.1 (d, ^{3}J(C,P) = 10.5 Hz; *m*-PhP), 129.2 (s; *m*-PhC_3), 129.5 (s; *o*-PhC_3), 130.5 (d, ^{4}J(C,P) = 1.3 Hz; C_6), 131.3 (d, ^{4}J(C,P) = 2.4 Hz; *p*-PhP), 132.3 (d, ^{1}J(C,P) = 36.1 Hz; *ipso*-PhP), 132.7 (d, ^{2}J(C,P) = 13.5 Hz; *o*-PhP), 133.8 (d, ^{3}J(C,P) = 6.9 Hz; *ipso*-PhC_3), 136.3 (d, ^{3}J(C,P) = 1.5 Hz; *ipso*-PhN), 137.9 (d, ^{1}J(C,P) = 52.8 Hz; C_9), 143.8 (d, ^{2}J(C,P) = 8.7 Hz; C_4), 145.6 (d, ^{1}J(C,P) = 47.1 Hz; C_2), 195.8 (d, ^{2}J(C,P) = 6.7 Hz, ^{1}J(C,W) = 125.6 Hz; *cis*-CO), 198.0 ppm (d, ^{2}J(C,P) = 21.8 Hz; *trans*-CO); ^{1}H NMR (250.1 MHz,$CDCl_3$): δ = 5.63 (d, ^{3}J(H,P) = 13.5 Hz, 2H; N*H*), 5.92 (s, 4H; Ph*H*N), 7.15–7.24 (m, 4H; C_5H, C_7H), 7.27–7.49 ppm (m, 24H; Ph*H*); IR (KBr): ν = 1933 (s/br, $C{=}O_{eq}$), 1985 (m, $C{=}O_{eq}$), 2072 (s, CO_{ax}); elemental analysis: calcd (%) for $C_{56}H_{34}N_2O_{10}P_2W_2$: C 50.78, H 2.59; found: C 50.47, H 2.61. **16b** (*meso*): mp ≥ 190 °C (decomp.); $^{31}P\{^{1}H\}$ NMR (101.3 MHz, $CDCl_3$): δ = 16.3 ppm (^{1}J(P,W) = 232.5 Hz); $^{13}C\{^{1}H\}$ NMR (62.9 MHz, $CDCl_3$): δ = 120.6 (s; *o*-PhN), 121.5 (d, ^{3}J(C,P) = 5.0 Hz; C_5), 125.7 (d, ^{3}J(C,P) = 10.3 Hz; C_7), 127.5 (d, ^{2}J(C,P) = 16.2 Hz; C_3), 128.2 (s; *p*-PhC_3), 128.7 (d, ^{2}J(C,P) = 14.2 Hz; C_8), 129.1 (d, ^{3}J(C,P) = 10.5 Hz; *m*-PhP), 129.2 (s; *m*-PhC_3), 129.6 (s; *o*-PhC_3), 130.5 (d, ^{4}J(C,P) = 1.3 Hz; C_6), 131.3 (d, ^{4}J(C,P) = 2.4 Hz; *p*-PhP), 132.4 (d, ^{1}J(C,P) = 36.4 Hz; *ipso*-PhP), 132.8 (d, ^{2}J(C,P) = 13.5 Hz; *o*-PhP), 133.8 (d, ^{3}J(C,P) = 6.9 Hz; *ipso*-PhC_3), 136.4 (d, ^{3}J(C,P) = 1.6 Hz; *ipso*-PhN), 138.0 (d, ^{1}J(C,P) = 53.0 Hz; C_9), 143.9 (d, ^{2}J(C,P) = 8.7 Hz; C_4), 145.9 (d, ^{1}J(C,P) = 47.1 Hz; C_2), 195.8 (d, ^{2}J(C,P) = 6.7 Hz, ^{1}J(C,W) = 125.7 Hz; *cis*-CO), 198.0 ppm (d, ^{2}J(C,P) = 21.8 Hz; *trans*-CO); ^{1}H NMR (250.1 MHz, $CDCl_3$): δ = 5.65 (d, ^{3}J(H,P) = 13.5 Hz, 2H; N*H*), 5.92 (s, 4H; Ph*H*N), 7.15–7.24 (m, 4H; C_5H, C_7H), 7.27–7.53 ppm (m, 24H; Ph*H*); IR (KBr): ν = 1923 (s/br, $C{=}O_{eq}$), 1985 (m, $C{=}O_{eq}$), 2070 (s, $C{=}O_{ax}$).

1,3-Diphenyl-2-phenylamino-1*H*-phosphindole (20): Complex **14a** (156 mg, 0.22 mmol) and dppe (97 mg, 0.24 mmol) were stirred in refluxing xylene (8 mL) for 60 h. Evaporation to dryness and chromatography over neutral aluminum oxide with pentane/dichloromethane (4/1) as eluent gave **20** (70 mg, 84 %) as a yellow solid. **20**: mp 249-251 °C; $^{31}P\{^{1}H\}$ NMR (101.3 MHz, $CDCl_3$): δ = – 7.4 ppm; $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 118.2 (d, ^{4}J(C,P) = 8.3 Hz; *o*-PhN), 120.4 (d, ^{3}J(C,P) = 0.8 Hz; C_5), 121.3 (d, ^{6}J(C,P) = 0.5 Hz; *p*-PhN), 123.9 (d, ^{3}J(C,P) = 8.7 Hz; C_7), 126.2 (d, ^{2}J(C,P) = 7.5 Hz; C_3), 127.6 (s; *p*-PhC_3), 128.6 (s; C_6), 128.6 (d, ^{3}J(C,P) = 7.9 Hz; *m*-PhP), 129.0 (s; *m*-PhN), 129.3 (s; *o*-PhC_3), 129.3 (d, ^{2}J(C,P) = 23.2 Hz; C_8), 129.4 (d, ^{4}J(C,P) = 1.3 Hz; *p*-PhP), 129.8 (d, ^{5}J(C,P) = 1.5 Hz; *m*-PhC_3), 133.1 (d, ^{2}J(C,P) = 19.7 Hz; *o*-PhP), 134.0 (d, ^{1}J(C,P) = 17.1 Hz; *ipso*-PhP), 134.9 (d, ^{3}J(C,P) = 0.7 Hz; *ipso*-PhC_3), 136.6 (d, ^{1}J(C,P) = 1.8 Hz; C_9), 143.1 (s; *ipso*-PhN), 147.1 (d, ^{2}J(C,P) = 1.6 Hz; C_4), 148.7 ppm (d, ^{1}J(C,P) = 6.8 Hz; C_2); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 6.13 (br. d, ^{3}J(H,P) = 10.3 Hz, 1H; N*H*),

6.82–6.89 (m, 1H; *p*-Ph*H*N), 7.05–7.18 (m, 6H; C_5H, C_7H, *o*-Ph*H*N, *m*-Ph*H*N), 7.18–7.29 (m, 4H; C_6H, *m*-Ph*H*P, *p*-Ph*H*P), 7.31–7.36 (m, 2H; *o*-Ph*H*P), 7.36–7.42 (m, 1H; *p*-Ph*H*C), 7.45–7.55 ppm (m, 5H; C_8H, *m*-Ph*H*C, *o*-Ph*H*C); HR-MS (EI, 70 eV): *m/z* (%): 377 (100) $[M]^+$; calcd for $C_{26}H_{20}NP$: 377.13333; found: 377.13563.

Reaction of $Fe(CO)_4$–complexed phosphirane 23 with 13a: 8 mL of a 1-hexene solution of **23** (0.1M, 0.8 mmol) and *N*-phenyl-diphenylketenimine (**13a**) (0.24 g, 0.88 mmol) were heated at 40 °C for 60 hours. Evaporation to dryness and chromatography of the residue over neutral aluminum oxide with pentane/dichloromethane (9/1) as eluent gave **25** (0.13 g, 29%) and **26** (0.13 g, 29%) both as an orange oil. Crystallization from pentane at – 20 °C afforded yellow crystals of **26**.

(1-diisopropylamino-2-phenylamino-3-phenyl-1*H*-phosphindole)tetracarbonyliron (25): $^{31}P\{^1H\}$ NMR (101.3 MHz, C_6D_6): δ = 112.3 ppm; $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6): δ = 24.0 (d, ^3J(C,P) = 3.2 Hz; CH_3), 24.1 (d, ^3J(C,P) = 2.8 Hz; CH_3), 51.6 (d, ^2J(C,P) = 5.9 Hz; $CH(CH_3)_2$), 117.9 (s; *m*-PhN), 121.4 (s; *p*-PhN), 121.8 (d, ^3J(C,P) = 7.2 Hz; C_5), 126.1 (d, ^3J(C,P) = 10.7 Hz; C_7), 127.7 (s; *p*-Ph), 128.2 (d, ^2J(C,P) = unresolved; C_3), 128.4 (s; *o*-PhN), 128.5 (s; *m*-Ph), 128.8 (d, ^2J(C,P) = 12.7 Hz; C_8), 129.2 (s; *o*-Ph), 131.6 (d, ^4J(C,P) = 1.8 Hz; C_6), 134.9 (d, ^3J(C,P) = 10.0 Hz; *ipso*-Ph), 136.1 (d, ^1J(C,P) = 60.9 Hz; C_9), 141.1 (d, ^3J(C,P) = 5.8 Hz; *ipso*-PhN), 141.3 (d, ^2J(C,P) = 15.0 Hz; C_4), 142.8 (d, ^1J(C,P) = 65.0 Hz; C_2), 213.8 ppm (d, ^2J(C,P) = 17.8 Hz; *C*O); ^{1}H NMR (400.1 MHz, C_6D_6): δ = 1.01 (d, ^3J(H,H) = 6.9 Hz, 6H; CH_3), 1.09 (d, ^3J(H,H) = 6.9 Hz, 6H; CH_3), 4.05 (dsp, ^3J(H,H) = 6.9 Hz, ^3J(H,P) unresolved, 2H; $CH(CH_3)_2$), 5.87 (d, ^3J(H,P) = 4.6 Hz, 1H; N*H*), 6.53–6.61 (m, 3H; *m*- and *p*-Ph*H*N), 6.76–6.81 (m, 2H; *o*-Ph*H*N), 6.87–7.00 (m, 5H; C_6H, C_7H, *p*-Ph*H*, *m*-Ph*H*), 7.19–7.22 (m, ^3J(H,H) = 7.5 Hz, 1H; C_5H), 7.24–7.27 (m, 2H; *o*-Ph*H*), 7.78–7.83 ppm (m, ^3J(H,H) = 6.9 Hz, 1H; C_8H); IR (KBr): ν = 1927, 1942 (s/br, $C{=}O_{eq}$), 1973 (m, $C{=}O_{eq}$), 2047 (s, $C{=}O_{ax}$); HR-MS (EI, 70 eV): *m/z* (%): 568 (1) $[M]^+$, 540 (1) $[M - CO]^+$, 512 (1) $[M - 2CO]^+$, 484 (40) $[M - 3CO]^+$, 456 (18) $[M - 4CO]^+$, 400 (32) $[M - Fe(CO)_4]^+$, 357 (100) $[M - Fe(CO)_4 - C_3H_7]^+$; calcd for $C_{30}H_{29}N_2O_4P^{56}Fe$: 568.12140; found: 568.12253.

(1-diisopropylamino-2-diphenylmethylene-2,3-dihydro-1*H*-benzo[1,3]azaphosphole) tetracarbonyliron (26): mp ≥ 86 °C (decomp.); $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$): δ = 104.2 ppm; $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6): δ = 23.7 (d, ^3J(C,P) = 3.7 Hz; CH_3), 25.1 (d, ^3J(C,P) = 2.6 Hz; CH_3), 52.3 (d, ^2J(C,P) = 7.6 Hz; $CH(CH_3)_2$), 110.4 (d, ^3J(C,P) = 4.2 Hz; C_5), 120.5 (d, ^3J(C,P) = 10.3 Hz; C_7), 125.3 (d, ^1J(C,P) = 56.9 Hz; C_9), 127.3 (d, ^2J(C,P) unresolved; CPh_2), 127.6 (s; *p*-Ph), 127.9 (s; *ipso*-Ph), 128 (unresolved; C_2), 128.1 (s; *p*-Ph), 128.4 (s; *ipso*-Ph), 128.8 (s; *m*-Ph), 129.6 (s; *m*-Ph), 129.6 (s; *o*-Ph), 130.0 (d, ^2J(C,P) = 12.1 Hz; C_8), 131.2 (s; *o*-Ph), 132.0 (d, ^4J(C,P) = 1.5 Hz; C_6), 143.2 (d, ^2J(C,P) = 5.6 Hz; C_4), 213.5 ppm (d, ^2J(C,P) = 17.8 Hz; *C*O); ^{1}H NMR (400.1 MHz, C_6D_6): δ = 1.08 (d, ^3J(H,H) = 6.9 Hz, 6H; CH_3), 1.12 (d, ^3J(H,H) = 6.9 Hz, 6H; CH_3), 4.12 (dsp, ^3J(H,H) = 6.9 Hz, ^3J(H,P) unresolved, 2H; $CH(CH_3)_2$), 5.70 (dd, ^3J(H,H) = 8.2 Hz, ^4J(H,P) = 2.9 Hz, 1H; C_5H), 6.28 (d, ^3J(H,P) = 4.9 Hz, 1H; N*H*), 6.63

(m, ^3J(H,H) = 7.5 Hz, ^4J(H,P) = 3.2 Hz, 1H; C_7H), 6.83 (m, ^3J(H,H) = 7.7 Hz, 1H; C_6H), 7.02–7.04 (m, 1H; *p*-Ph*H*), 7.08–7.15 (m, 3H; *p*-Ph*H*, *m*-Ph*H*), 7.17–7.22 (m, 2H; *m*-Ph*H*), 7.32–7.35 (m, 2H; *o*-Ph*H*), 7.51–7.54 (m, 2H; *o*-Ph*H*), 7.85 ppm (dd, ^3J(H,H) = 7.6 Hz, ^3J(H,P) = 7.9 Hz, 1H; C_8H); IR (KBr): ν = 1917, 1935 (s/br, $C{=}O_{eq}$), 1973 (m, $C{=}O_{eq}$), 2047 (s, $C{=}O_{ax}$); HR-MS (EI, 70 eV): *m/z* (%): 400 (20) $[M - Fe(CO)_4]^+$, 300 (100) $[M - Fe(CO)_4 - N(C_3H_7)_2]^+$; calcd for $C_{26}H_{29}N_2P$ ($M - Fe(CO)_4$): 400.20682; found: 400.20761.

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Reflections up to a resolution of $(\sin \theta/\lambda)_{max}$ = 0.65 Å^{-1} were measured on a Nonius KappaCCD diffractometer with rotating anode and graphite monochromator (λ = 0.71073 Å) at a temperature of 150(2) K. An analytical absorption correction was applied (μ = 4.624 mm^{-1}, 0.30-0.52 correction range). 5861 Reflections were unique (R_{int} = 0.0580). The structure was solved with automated Patterson Methods[71] and refined with SHELXL-97[72] on F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were introduced in calculated positions and refined as rigid groups. One phenyl residue was disordered over two orientations. 366 Parameters were refined with 186 restraints. R1/wR2 [I > 2σ(I)]: 0.0242/0.0535. R1/wR2 [all refl.]: 0.0356/0.0574. S = 1.071. Residual electron density between -0.94 and 1.58 e/Å^3. Geometry calculations, drawings and checking for higher symmetry were performed with the PLATON[73] package. CCDC-264309 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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[41] Three other isomers, namely *gauche***30** (–936.7217306 a.u.), *anti***31** (–936.7569504 a.u.) and *gauche***32** (–936.7569217 a.u.), were also found on the potential energy surface, but show similar reaction energies, respectively 47.3, 69.4 and 69.4 kcal·mol^{-1}.

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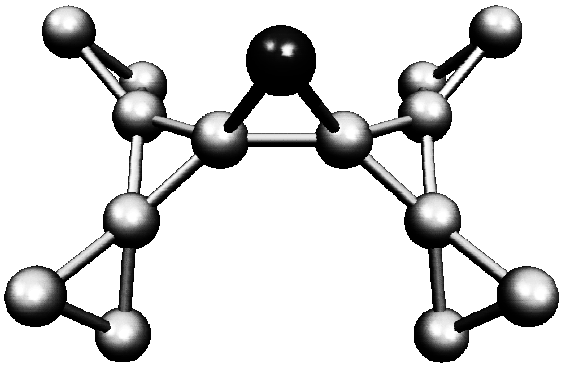
Branched Phospha[7]triangulanes

3

A highly strained, thermally stable (up to 150 °C) branched phospha[7]triangulane (see picture) was synthesized from the second-generation bicyclopropylidene and transient phosphinidene Ph-P=$W(CO)_5$, followed by demetallation in refluxing xylene. Bulkier transient CuCl–alkene-complexed phosphinidene gave 2-phosphabicyclo-[3.2.0]hept-1(5)-ene as an additional product. The outer sphere spirocyclopropanes provide a stabilizing factor for both of these novel compounds.

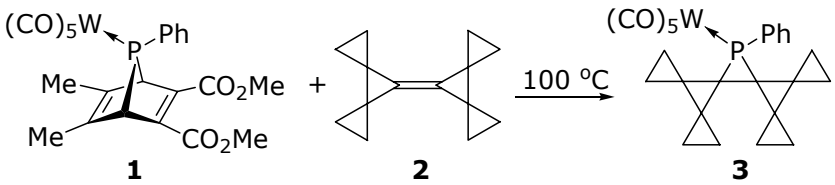


Published in: *J. Am. Chem. Soc.* **2004**, *126*, 3050–3051.

3.1 Introduction

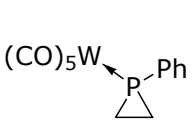
Strain gives cyclopropane derivatives their unique electronic and chemical properties.[1] Spirofusion of three-membered rings augments the strain by 8.5 kcal·mol^{-1},[2] and yet many stable linear and branched [*n*]triangulanes are known,[3,4] but instead only few hetero[*n*]triangulanes are known, irrespective of whether it concerns spirocyclopropanated aziridines, oxiranes, thiiranes, siliranes, or phosphiranes.[3] The higher reactivity of the heterocyclic ring is believed to be the underlying cause. In contrast, we now report on the exceptional stability of a branched phospha[7]triangulane.

3.2 Phospha[7]triangulanes

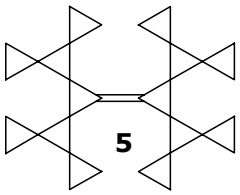


Scheme 1. Synthesis of Phospha[7]triangulane Complex **3**.

Reaction of carbene-like terminal phosphinidene complex Ph-P=W(CO)$_5$,[5] generated in situ by cheletropic elimination from **1** at 100 °C in toluene, with second-generation bicyclopropylidene **2**[4] afforded W(CO)$_5$-complexed phospha[7]triangulane **3** (mp 178–179 °C, 88%) as the sole product (Scheme 1). Its ^{31}P NMR resonance at δ –119.6 is deshielded by 9.8 from the first-generation triangulane[6] and by 70.5 ppm from parent **4**.[7] This illustrates that the second spirocyclopropane sphere has little influence. Attempted synthesis of the larger phospha[15]triangulane from the third-generation bicyclopropylidene **5**[4] failed, because the double bond of **5** is too congested.[4b]

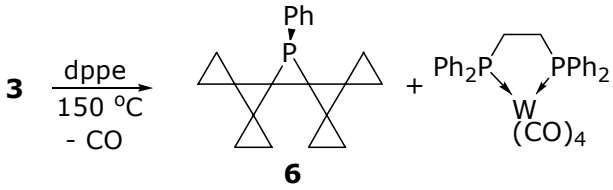


4



5

The stabilizing $W(CO)_5$ group was subsequently removed from **3**. While oxidation with iodine at –30 °C[8] afforded $[W(CO)_4I]^+I^-$ complexed phospha[7]triangulane ($\delta^{31}P$ –130.1), quenching with *N*-methylimidazole[8] only led to degradation. Instead direct ligand exchange in refluxing xylene (150 °C!) with $(Ph_2PCH_2)_2$ (dppe)[9] was more successful, giving free phospha[7]triangulane **6** (mp 168–169 °C, 82%) as the sole product (Scheme 2).[10] Its $\delta^{31}P$ at –164.0 shows the expected shielding on demetallation and the increased $^1J(P,C)$ coupling from 6.2 (**3**) to 37.3 Hz resembles that for the parent 1-phenylphosphirane.[7,11] The molecules of **6** are located on an exact mirror plane in the crystal (Figure 1)[12] and show slightly elongated P–C and P–Ph bonds (by respectively 0.02 and 0.01 Å) due to the absence of the stabilizing $W(CO)_5$ group.



6

Scheme 2. Decomplexation of **3**.

The exceptional thermal stability of **3** and **6** is remarkable as most phosphiranes eliminate or transfer Ph-P=$W(CO)_5$ at much lower temperatures (≤ 100–115 °C).[10] That the six spirofused rings indeed stabilize the CCP ring is evident from the mere 6.5 kcal·mol^{-1} difference in strain energies (SE), determined with homodesmotic reactions at G3(MP2),[13] between parent phospha[7]triangulane **6'** (H for Ph; 224.2 kcal·mol^{-1}) and alkene **2** (217.7 kcal·mol^{-1}); phosphirane C_2PH_5 has an SE of 20.8 kcal·mol^{-1}. A contributing factor is the release of olefin strain (OS) in **2** that amounts to 23.1 kcal·mol^{-1}. The higher stability of **6** is also related to a higher olefinic π-donor and π^*-acceptor ability in **2**[4] caused by spirocyclopropanation, which is reflected in

the 9.3 kcal·mol^{-1} larger exothermicity for reaction of ^{1}PH (A_1) with **2** (82.9 kcal·mol^{-1}) than for ^{1}PH with ethylene (73.5 kcal·mol^{-1}; G3(MP2)). This behavior is in line with a higher HOMO (–8.45 vs –10.08 eV) and a lower LUMO (4.12 vs 4.88 eV) for **2** when compared to ethylene.[14]

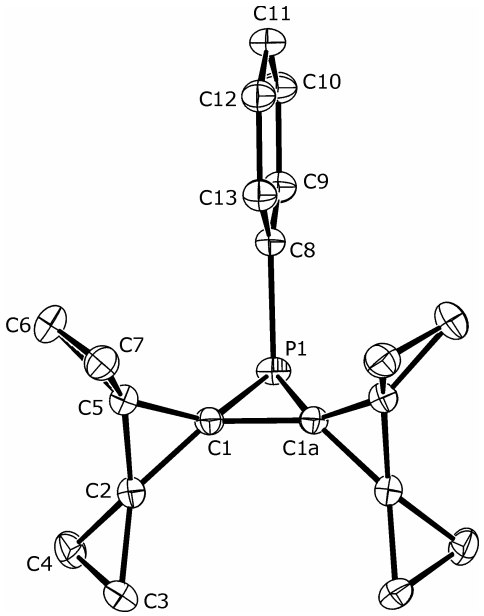
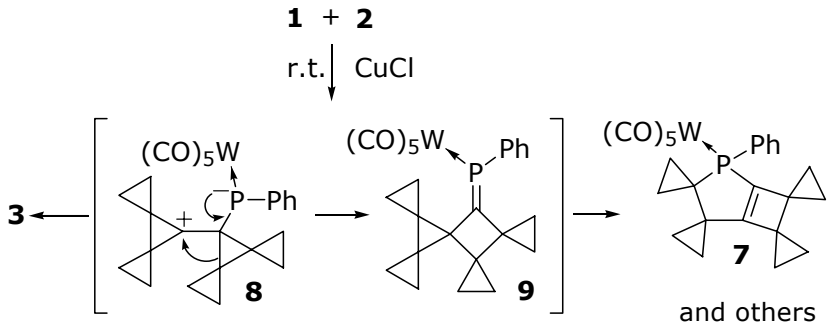


Figure 1. Displacement ellipsoid plot (50%) of **6**. Selected bond lengths [Å] and angles [deg]: P1–C1 1.8430(11), C1–C1a 1.470(2), C1–C2 1.4889(14), C1–C5 1.4879(14), C2–C3 1.4862(15), C2–C4 1.4825(15), C2–C5 1.4712(15), C3–C4 1.5305(17), C5–C6 1.4841(15), C5–C7 1.4869(16), C6–C7 1.5262(18); C1–P1–C1a 47.02(6), P1–C1–C1a 66.49(3). A: *x*, 0.5 – *y*, *z*.

3.3 Influence of CuCl

The higher reactivity of alkene **2** is also reflected in the CuCl-catalyzed reaction with **1**,[15] but with surprises. Not only does the reaction already take place at room temperature, instead of the usual 55–60 °C,[15] but it also gave a modest yield of **3** (42%) besides other products, including **7** (6%) (Scheme 3).[16] The structure of **7**, the first 2-phosphabicyclo[3.2.0]hept-1(5)-ene derivative,[17] spirocyclopropanated at each carbon, was established by single-crystal X-ray crystallography (Figure 2).[12]



Scheme 3. Formation of **3** and **7** under CuCl catalysis.

The formation of **7** is attributed to the influence of CuCl on the cycloaddition process as **3** converts with added CuCl only slowly in refluxing toluene to **7** and other products. This CuCl-catalyzed cycloaddition behavior concurs with a recent analysis suggesting that a CuCl-alkene complex facilitates the fragmentation of **1** to give a reactive [PhP(Cl)W(CO)$_5$]–Cu–alkene intermediate that subsequently undergoes an S_N2-type addition with alkenes.[18] This bulky Cu-containing reagent likely hampers the concerted [1+2]-cycloaddition, thereby enabling the formation of zwitterion **8**, which can ring-close to **3** but also rearrange to **9** in analogy to the cyclopropanation reaction of **2** with N_2CHCO_2Et in which both products were obtained.[4b] However, contrasting its stable hydrocarbon analogue, the more reactive P=C bond of **9** enables a subsequent [1,3]-sigmatropic shift[19] to give **7**. This conversion is 19.9 kcal·mol^{-1} exothermic at B3LYP/6-31G* for the parent system (H for Ph, no W(CO)$_5$).[20]

3.4 Conclusion

A highly strained, thermally stable (up to 150 °C) branched phospha[7]triangulane was synthesized from second-generation bicyclopropylidene **2** and phosphinidene Ph-P=W(CO)$_5$, followed by demetallation in refluxing xylene. Bulkier transient CuCl–alkene–complexed phosphinidene gave also a 2-phosphabicyclo[3.2.0]hept-1(5)-ene. Spirocyclopropane-annelation is stabilizing both of these novel compounds.

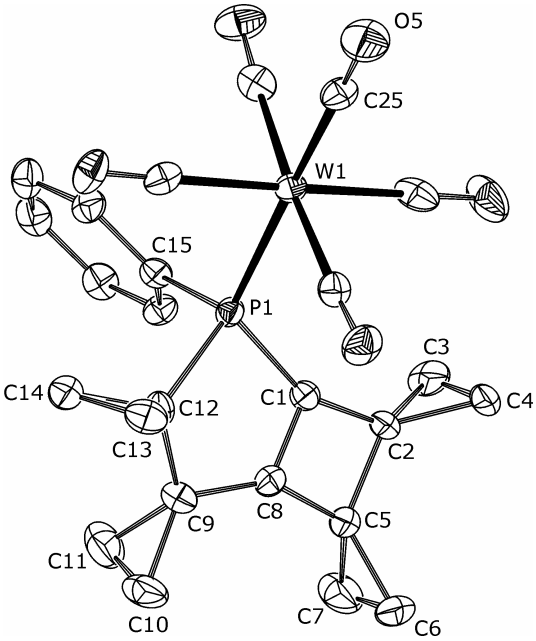
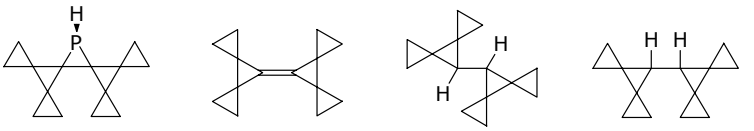


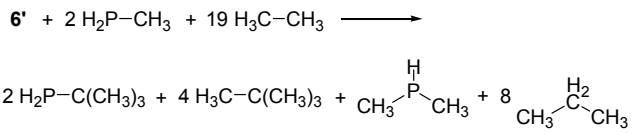
Figure 2. Displacement ellipsoid plot (50%) of **7** (molecule one of two). Selected bond lengths [Å], angles and torsion angles [°]; the values for the second molecule are in square brackets: W1-P1 2.5178(14) [2.5090(14)], P1-C1 1.805(7) [1.792(7)], P1-C12 1.876(6) [1.868(4)], C1-C2 1.495(8) [1.530(8)], C1-C8 1.338(8) [1.330(9)], C2-C5 1.524(8) [1.554(9)], C5-C8 1.488(7) [1.500(9)], C8-C9 1.481(8) [1.473(8)], C9-C12 1.539(8) [1.527(8)]; C1-P1-C12 89.2(2) [89.1(2)], P1-C1-C8 112.4(4) [112.6(4)], C2-C1-C8 92.6(5) [93.4(5)], C1-C8-C5 94.6(5) [95.1(5)]; C12-P1-C1-C8 11.6(3) [9.0(4)], C1-C8-C9-C12 –14.8(5) [-15.5(6)].

3.5 Computational Section

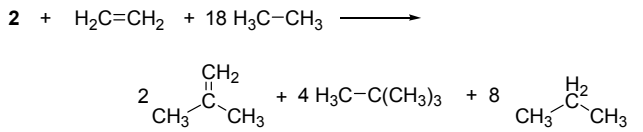


6' **2** **2-H_2-*trans*** **2-H_2-*cisoid***

Ring strain. We calculated the strain energy for the parent branched phospha[7]triangulane **6'** (H instead of Ph, C_s symmetry) and its precursor, the second generation bicyclopropylidene **2** (D_{2h} symmetry), at the G3(MP2) level of theory[13] using homodesmotic reactions[26] (eqn. 1,2).



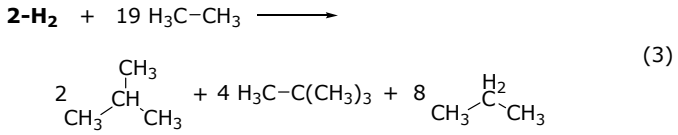
(1)



(2)

The MP2-optimized geometry of **6'** compares favorably with the X-ray structure of the phenyl-substituted **6**. **6'** has slightly longer P-C bonds (0.02 Å), a shorter central C-C bond (0.015 Å) and a slightly tighter CPC bond angle (1°). The strain energy (SE) and heat of formation (ΔH_f^o) of **6'** were determined with homodesmotic eq. 1 at G3(MP2) to give large values of 228.3 and 199.8 kcal·mol^{-1}, respectively; the corresponding values for the hydrocarbon **2** (eq. 2) are 217.7 and 200.1 kcal·mol^{-1}.

Olefin strain. Olefin strain (OS) is calculated by substracting the total strain energy of the most stable conformer of the parent hydrocarbon from the total strain energy of the olefin, also in the most stable conformation.[27] To obtain the olefin strain in **2** we calculated the strain energy for the hydrogenated second generation bicyclopropylidene **2**-**H$_2$**-*trans* (C_{2h} symmetry) and **2**-**H$_2$**-*cisoid* (HCCH = 53.7°), at the G3(MP2) level of theory using homodesmotic reactions (eqn. 3). We found that **2**-**H$_2$**-*cis* (C_{2v} symmetry) is an transition state and not a minimum. The **2**-**H$_2$**-*cisoid* structure is the energetically most favorable structure and was used for determining the olefin strain in **2**.



(3)

Olefin strain[27] in **2** = SE (**2**) – SE (**2**-**H$_2$**-*cisoid*) = 217.72 – 194.58 = 23.14 kcal·mol^{-1}. (Olefin strain[27] in **2** = SE (**2**) – SE (**2**-**H$_2$**-*trans*) = 217.72 – 194.69 = 23.03 kcal·mol^{-1}.)

3.6 Experimental Section

All experiments were performed under an atmosphere of dry nitrogen. Solvents were purified, dried, and degassed by standard techniques. NMR spectra were recorded (298K) on Bruker Advance 250 (^{31}P; 85% H_3PO_4) and MSL 400 (^{1}H, ^{13}C) spectrometers, internally referenced to

residual solvent resonances. High-resolution mass spectra (HR-MS) were recorded on a Finnigan Mat 900 and IR spectra on a Mattson 6030 Galaxy spectrophotometer. Melting points were measured on samples in unsealed capillaries and are uncorrected. Compound **1**[21] and **2**[4] were synthesized according to literature procedures.

(15-Phenyl-15-phosphahexaspiro[2.0.2.0.0.0.2.0.2.0.1]pentadec-15-yl)pentacarbonyltungsten (3): Complex **1** (0.59 g, 0.90 mmol) and **2** (0.20 g, 1.08 mmol) were heated at 100 °C for 12 h in toluene (5 mL). Evaporation to dryness and chromatography of the residue over silica with pentane/dichloromethane (19/1) yielded **3** (0.49 g; 88 %) as a colorless solid: m.p. 178–179 °C (decomp); $^{31}P\{^{1}H\}$ NMR (101.3 MHz, $CDCl_3$): δ = – 119.6 (^{1}J(P,W) = 250.1 Hz); $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 4.4 (d, ^{3}J(C,P) = 4.0 Hz; *C*H_2), 4.7 (d, ^{3}J(C,P) = 3.3 Hz; *C*H_2), 7.1 (d, ^{3}J(C,P) = 2.1 Hz; *C*H_2), 7.4 (s; *C*H_2), 21.8 (d, ^{2}J(C,P) = 5.3 Hz; PC*C*), 21.9 (d, ^{2}J(C,P) = 1.2 Hz; PC*C*), 34.5 (d, ^{1}J(C,P) = 6.2 Hz; P*C*), 128.2 (d, ^{3}J(C,P) = 10.2 Hz; *m*-Ph), 130.0 (d, ^{4}J(C,P) = 2.6 Hz; *p*-Ph), 131.9 (d, ^{2}J(C,P) = 13.1 Hz; *o*-Ph), 132.9 (d, ^{1}J(C,P) = 19.9 Hz; *ipso*-Ph), 195.9 (d, ^{2}J(C,P) = 8.3, ^{1}J(C,W) = 125.4 Hz; *cis*-CO), 198.9 (d, ^{2}J(C,P) = 29.5 Hz; *trans*-CO); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.60–0.68 (m, 4H; C*H*$_2$), 0.75–0.80 (m, 2H; C*H*$_2$), 0.85–0.96 (m, 6H; C*H*$_2$), 0.96–1.02 (m, 2H; C*H*$_2$), 1.22–1.28 (m, 2H; C*H*$_2$), 7.25–7.39 (m, 5H; Ph*H*); IR (KBr): ν = 1923, 1942 (s/br, CO_{eq}), 1985 (w, CO_{eq}), 2072 cm^{-1} (m, CO_{ax}); HR-MS (EI, 70 eV): *m/z* (%): 616 (4) $[M]^+$; calcd for $C_{25}H_{21}O_5PW$: 616.06366, found: 616.06655.

(15-Phenyl-15-phosphahexaspiro[2.0.2.0.0.0.2.0.2.0.1]pentadecane (6): Complex **3** (70 mg, 0.11 mmol) and dppe (67 mg, 0.17 mmol) were heated in refluxing xylene (2 mL) for 48 h. Evaporation to dryness and chromatography over silica with pentane/dichloromethane (19/1) yielded **6** (26 mg, 82 %) as a colorless solid: m.p. 168–169 °C. $^{31}P\{^{1}H\}$ NMR (101.3 MHz, $CDCl_3$): δ = – 164.0. $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 3.5 (d, ^{3}J(C,P) = 1.8 Hz, *C*H_2), 5.9 (d, ^{3}J(C,P) = 1.8 Hz, *C*H_2), 7.3 (d, ^{3}J(C,P) = 1.7 Hz, *C*H_2), 7.7 (d, ^{3}J(C,P) = 1.1 Hz, *C*H_2), 21.1 (d, ^{1}J(C,P) = 2.2 Hz, PC*C*), 21.4 (d, ^{2}J(C,P) = 9.7 Hz, PC*C*), 34.9 (d, ^{1}J(C,P) = 37.3 Hz, P*C*), 127.7 (d, ^{3}J(C,P) = 7.3 Hz, *m*-Ph), 128.3 (d, ^{4}J(C,P) = 1.3 Hz, *p*-Ph), 132.9 (d, ^{2}J(C,P) = 20.5 Hz, *o*-Ph), 136.2 (d, ^{1}J(C,P) = 43.6 Hz, *ipso*-Ph). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.49–0.54 (m, 2H, C*H*), 0.69–0.76 (m, 4H, C*H*, C*H*$_2$), 0.83–0.91 (m, 6H, C*H*$_2$), 0.93–0.99 (m, 2H, C*H*), 1.01–1.07 (m, 2H, C*H*), 7.07–7.11 (m, 2H, *o*-Ph*H*), 7.15–7.20 (m, 2H, *m*-Ph*H*), 7.21–7.26 (m, 1H, *p*-Ph*H*). HR-MS (EI, 70 eV): *m/z* (%): 291 (52) $[M - H]^+$; calcd for $C_{20}H_{20}P$ (M-H): 291.13025, found: 291.13138.

{2-Phenyl-2-phospha-3:3,4:4,6:6,7:7-tetrakisethanobicyclo[3.2.0]hept-1(5)-en-2-yl}-pentacarbonyltungsten (7): Complex **1** (0.65 g, 1.00 mmol), **2** (0.22 g, 1.20 mmol) and CuCl (10 mg, 0.1 mmol) were stirred at RT for 20 h in toluene (4 mL). Evaporation to dryness and chromatography of the residue over silica with pentane/dichloromethane (19/1) yielded **3** (0.26 g, 42 %) and **7** (40 mg, 6 %), both as a pale yellow solid. Crystallization of **7** from diethyl ether

at – 5 °C afforded colorless crystals: m.p. 146–148 °C; ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.23–0.29 (m, 1H; CH_2), 0.33–0.42 (m, 2H; CH_2), 0.51–0.59 (m, 2H; CH_2), 0.61–0.71 (m, 6H; CH_2), 0.79–0.83 (m, 2H, CH_2) 0.91–0.98 (m, 2H; CH_2), 1.10–1.14 (m, 1H, CH_2), 7.40–7.44 (m, 3H; *m*-Ph*H*, *p*-Ph*H*), 7.50–7.56 (m, 2H; *o*-Ph*H*); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ = 6.3, 6.6, 7.7, 7.8, 7.9, 8.8 (s; *C*H_2), 10.1 (d, ^{2}J(C,P) = 2.9 Hz; PC*C*H_2), 10.4 (d, ^{2}J(C,P) = 7.1 Hz; PC*C*H_2), 30.6 (d, ^{2}J(C,P) = 7.7 Hz; PC*C*), 34.9 (d, ^{1}J(C,P) = 39.7 Hz; P*C*), 35.2 (d, ^{2}J(C,P) = 22.1 Hz; P(C=)*C*), 35.8 (d, ^{3}J(C,P) = 4.2 Hz; PC=C*C*), 128.5 (d, ^{3}J(C,P) = 9.6 Hz; *m*-Ph), 130.3 (d, ^{4}J(C,P) = 2.1 Hz; *p*-Ph), 131.4 (d, ^{2}J(C,P) = 12.3 Hz; *o*-Ph), 136.3 (d, ^{1}J(C,P) = 32.5 Hz; *ipso*-Ph), 142.5 (d, ^{1}J(C,P) = 31.2 Hz; P*C*=C), 172.0 (d, ^{2}J(C,P) = 5.8 Hz; PC=*C*), 196.8 (d, ^{2}J(C,P) = 7.1, ^{1}J(C,W) = 125.4 Hz; *cis*-CO), 199.3 (d, ^{2}J(C,P) = 21.1 Hz; *trans*-CO); ^{31}P{^{1}H} NMR (101.3 MHz, $CDCl_3$): δ = 34.4 (^{1}J(P,W) = 238.4 Hz); IR (KBr): ν = 1908, 1933 (s/br, CO_{eq}), 1977 (w, CO_{eq}), 2068 cm^{-1} (m, CO_{ax}); HR-MS (EI, 70 eV): *m/z* (%): 616 (2) [*M*]$^{+}$; calcd for $C_{25}H_{21}O_5PW$: 616.06366, found: 616.06445.

3.7 References and Notes

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[12] Crystal structure determinations: X-ray intensities were measured on a Nonius KappaCCD diffractometer with rotating anode (λ=0.71073 Å). The structures were solved with direct methods[22] (compound **6**) or automated Patterson methods[23] (compound **7**) and refined with SHELXL-97[24] against F2 of all reflections. Molecular illustration, structure checking and calculations were performed with the PLATON package.[25] **6**: C20H21P, Fw = 292.34, colorless needle, 0.46 x 0.36 x 0.09 mm3, temperature = 150(2) K, monoclinic, *P*21/*m* (No. 11), *a* = 7.8462(1), *b* = 12.9734(2), *c* =8.7058(1) Å, β = 115.6968(6)°, *V* = 798.537(18) Å3, *Z* = 2, *D*x = 1.216 g/cm3. No absorption correction (μ = 0.164 mm-1). 15383 measured reflections, 1913 reflections were unique [(sinθ/λ)max = 0.65 Å-1]. 138 refined parameters. *R*-values [$I > 2\sigma(I)$]: R1= 0.0307, wR2 = 0.0784. *R*-values [all refl.]: R1= 0.0354, wR2 = 0.0812. GOF = 1.047. **7**: C25H21O5PW, Fw = 616.24, colorless plate, 0.09 x 0.09 x 0.03 mm3, temperature = 150(2) K, orthorhombic, *Pca*21 (no. 29), *a* = 18.9647(1), *b* = 11.3278(1), *c* =21.7733(2) Å, *V* = 4677.52(6) Å3, *Z* = 8, *D*x = 1.750 g/cm3. Analytical absorption correction (μ = 5.041 mm-1, 0.58-0.89 transmission). 80568 measured reflections, 10736 reflections were unique [(sinθ/λ)max = 0.65 Å-1]. 577 refined parameters. Flack parameter *x* = -0.022(5). *R*-values [$I > 2\sigma(I)$]: R1= 0.0285, wR2 = 0.0378. *R*-values [all refl.]: R1= 0.0450, wR2 = 0.0405. GOF = 0.975.

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for 7-(cyclopropylidene)dispiro-[2.0.2.1]heptane) (R. Gleiter, S. I. Kozhushkov, A. de Meijere, unpublished results).

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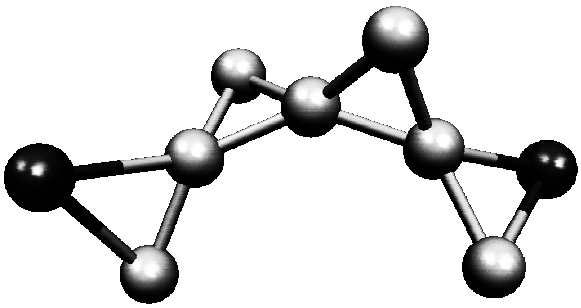
Linear and Branched Phospha[*n*]triangulanes

4

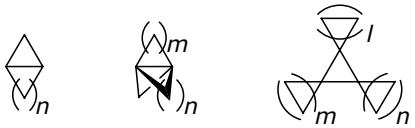
Novel, highly stable, linear and branched mono- and diphospha[*n*]triangulanes were synthesized in high yields by the CuCl-catalyzed phosphinidene addition to spirocyclopropanated methylenecyclopropanes and bicyclopropylidenes. The effect of spirofusion on the electronic properties of these aesthetically pleasing phosphacycles is apparent from X-ray single crystal structure analyses, which reveals a tightening of the phosphirane ring on additional spirocyclopropanation, and from the NMR features that show deshielded chemical signals for the ring-phosphorus and -carbon atoms. Steric factors play a role in the addition reaction when the substrate alkene carries a second sphere of spirocyclopropane rings and causes the formation of 2-phospha-bicyclo[3.2.0]heptenes in small amounts.



Published in: *Chem, Eur. J.* **2005**, *11*, in press.

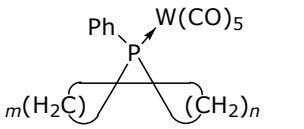
4.1 Introduction

The inherently strained cyclopropane derivatives have unique electronic and chemical properties due to their small valence angles and bent C–C bonds.[1] Embedding the three-membered ring into oligocycles by annelation or spirofusion with additional small rings augments the total strain to exceed that of the sum of the separate rings. This is well established not only for the ring-annelated bicyclic **1** and tricyclic propellane skeletons **2**, but also for the spirofused linear and branched so-called [*n*]triangulanes **3**.[2] The current record of a branched [15]triangulane[3] and linear [9]triangulane[3] exemplifies the accessibility of such extended arrays of spirofused cyclopropanes, which are surprisingly stable in spite of their high overall strain.

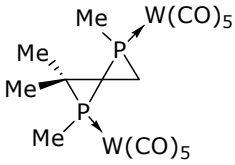


1 **2** **3**

By contrast to the large number of purely carbon-based triangulanes, far fewer spirocyclic compounds are known that contain a heteroatom, because of the higher reactivity of three-membered heterocycles.[2] Compounds with a phosphorus atom, that is a phosphirane ring,[4] such as 1-phosphaspiro[2,*n*]alkanes **4a-e**,[5] the 1-phosphadispiroalkanes **5a-d**,[6,7] and 1,4-diphosphaspiropentane **6**[8] became accessible by the [1+2]-cycloaddition of the in situ generated electrophilic phosphinidene complexes R-P=W(CO)$_5$ to the respective alkenes.[9,10]



4a-e *m = 0; n = 0,2–5*
5a-d *m = 2; n = 2–5*



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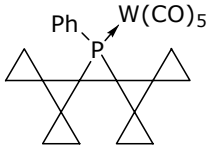
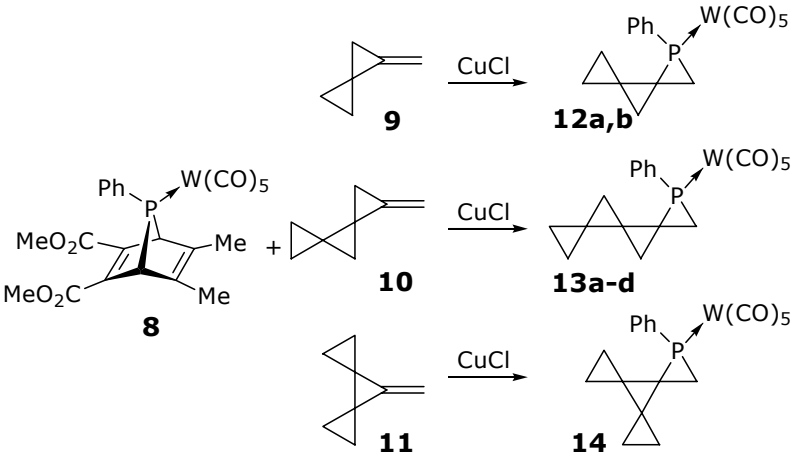


7

Recently, we described the synthesis of the first hetero[7]triangulane **7** and showed that even the demetallated compound is stable at 150 °C.[11] In the present report we expand on these earlier studies and describe a series of novel stable phospha[*n*]triangulanes containing one or two phosphorus atoms.

The syntheses of phospha[*n*]triangulanes (*n* = 3–5) was achieved by adding Ph-P=W(CO)$_5$ to terminal and non-terminal double bonds of spirocyclopropanated methylenecyclopropanes and bicyclopropylidenes, respectively. The influence of the CuCl catalyst on the addition reaction will also be addressed.



Scheme 1.

4.2 Spirocyclopropanated Methylenecyclopropanes

Reaction of Ph-P=W(CO)$_5$, generated in situ by the CuCl-catalyzed cycloreversion[12] of 7-phosphanorbornadiene complex **8**,[9,13] with methylenespiropentane (**9**) in toluene at 55 °C (1 h) gave in 78% yield, only the crystalline terminal phospha[3]triangulane complex **12** (Scheme 1) in a 5:4 ratio of the *anti* (**a**) and *syn* isomer (**b**). Figure 1 shows the X-ray crystal structure for the less congested *anti* isomer **12a**, where the P-W(CO)$_5$ group is *anti* to the terminal cyclopropane ring. The bond lengths of the phosphirane ring compare well with the values of the W(CO)$_5$-complexed smaller phospha[2]triangulane **4b**[5] (Table 1). Extending the number of cyclopropane rings to three, as in linear **10** or branched methylenetriangulane **11**, gave the corresponding linear and branched phospha[4]triangulanes **13** and **14** (Scheme 1). In the case of **14**, only one isomer can be formed (88%) of which the X-ray crystal structure is shown in Figure 1, but four diastereomers are feasible for linear **13** (94%), which depends on the *syn,anti* relationship of the phosphirane and terminal spirocyclopropane rings as well as that of the P-substituents. The less

congested two major isomers of the four observed by ^{31}P NMR spectroscopy (ratio 50:36:10:4) were fully characterized (see Experimental Section).

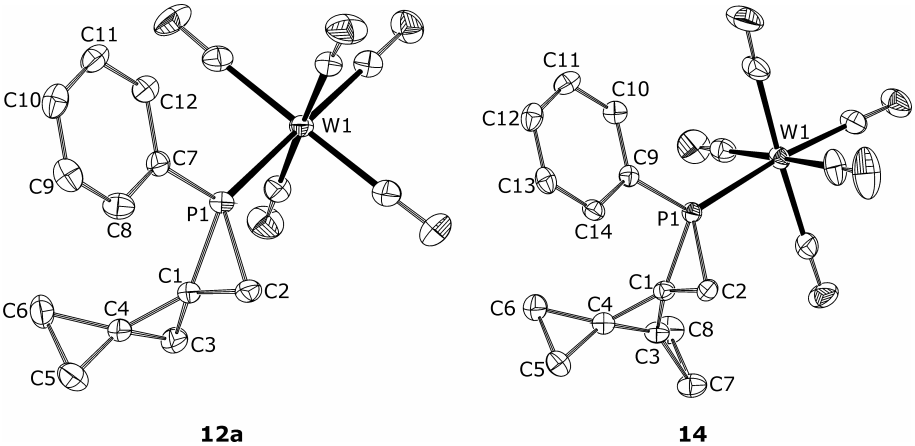
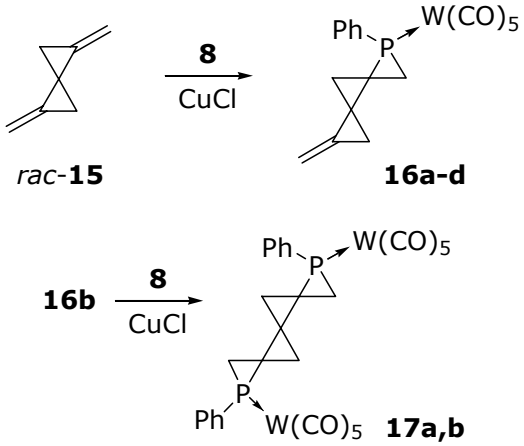


Figure 1. Displacement ellipsoid plot of **12a** (one of the two crystallographically independent molecules is shown) and **14** in the crystal with ellipsoids set at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]; the values for the second molecule are in square brackets. **12a**: C4-C5 1.486(4) [1.475(4)], C4-C6 1.478(4) [1.475(4)], C5-C6 1.528(4) [1.515(4)]; C1-P1-C2 48.41(11) [48.25(12)], C3-C1-C4 59.86(18) [60.33(18)], C5-C4-C6 62.1(2) [61.8(2)]. **14**: C3-C7 1.478(3), C3-C8 1.475(3), C4-C5 1.481(3), C4-C6 1.482(3), C5-C6 1.537(4), C7-C8 1.522(4); C1-P1-C2 48.36(10), C3-C1-C4 59.01(14), C5-C4-C6 62.50(17), C7-C3-C8 62.03(16).

Diphospha[4]triangulanes were accessible by using racemic 1,4-dimethylene-spiropentane *rac*-**15** as diene. Reaction of the phosphinidene precursor **8** (CuCl-catalyzed)[12] with only one double bond, with an excess of **15** in toluene at 55 °C (2 h), afforded 5-methylene-1-phosphadispiro[2.0.2.1]heptane **16** (Scheme 2) in 83% yield as a mixture of 4 diastereomers (^{31}P NMR: ratio 39:31:18:12) of which three could be fully characterized. The structure of the major *anti* isomer **16b**, separated by column chromatography, was ascertained by an X-ray crystal structure determination (Figure 2). The presence of the double bond (1.289(14) Å) is also evident from the ^{1}H-NMR resonances at δ = 5.36 (^{4}J(H,H) = 2.4 Hz) and 5.39 (^{4}J(H,H) = 1.8 Hz) and the ^{13}C-NMR resonances at δ = 101.6 (H_2C=) and 133.7 (=*C*).



Scheme 2.

Reaction of the remaining double bond in *anti*-**16b** with an excess of **8** (55 °C, CuCl, 3 h) resulted in the smooth formation of the novel linear diphospha[4]triangulane complex **17** in 78% yield in a 10:7 ratio of the *anti*,*anti* and *anti,syn* isomers (Scheme 2). *Anti*,*anti* isomer **17a** is easily recognized by its ^{31}P-NMR singlet (δ –147.9) and *anti*,*syn* isomer **17b** by its set of doublets (δ –150.4, –150.5; ^{4}J(P,P) = 4.5 Hz). Interestingly, the ^{13}C-NMR spectrum of **17a** displays an A_2X system for the central spiro-carbon atom at δ^{13}C = 25.4 (^{2}J(C,P) = 5.5 Hz). An X-ray crystal structure confirmed the assignment of this isomer (Figure 2).

Selected structural parameters of four of the novel (di)phospha[*n*]triangulane complexes are given in Table 1. The two different P–C bond distances (av. 1.796 and 1.846 Å) of their terminal phosphirane rings are similar to the values of the $W(CO)_5$-complexed smaller phospha[2]triangulane **4b**[5] with the distal bonds (remote to the spiro-carbon) being longer than the proximal ones (connected to the spiro-carbon). This effect of spirofusion is similar but more pronounced than in the all-carbon triangulanes[3,14] and is likewise due to rehybridization of the strained spiro-carbon, resulting in less s-character and thus elongation of the distal bonds.[2] The $PhPW(CO)_5$ group also affects the C1-spirofused cyclopropane ring, which also has proximal C–C bonds of different length (av. 1.503 and 1.468 Å) and a 1.493 Å (av.)

distal bond. The C1–C2 bonds (av. 1.498 Å) of all the structures are of similar length, as was reported for the parent 1-phenylphosphirane **4a**.[5]

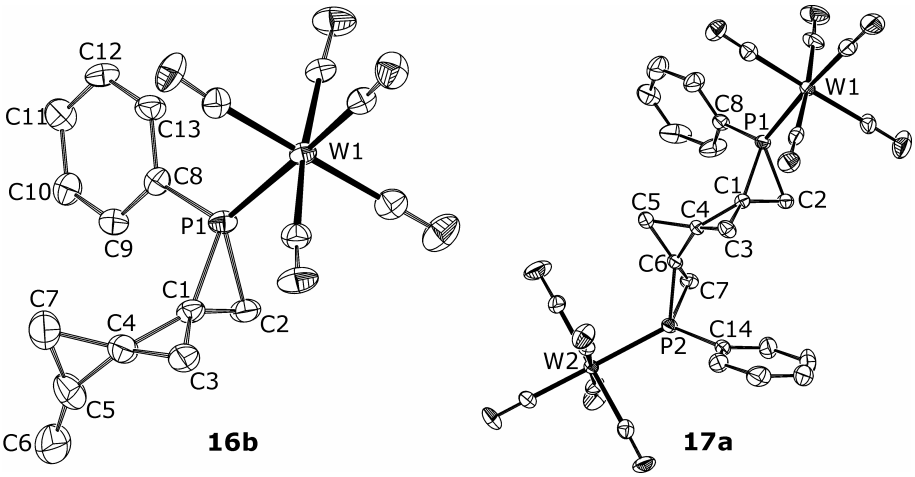
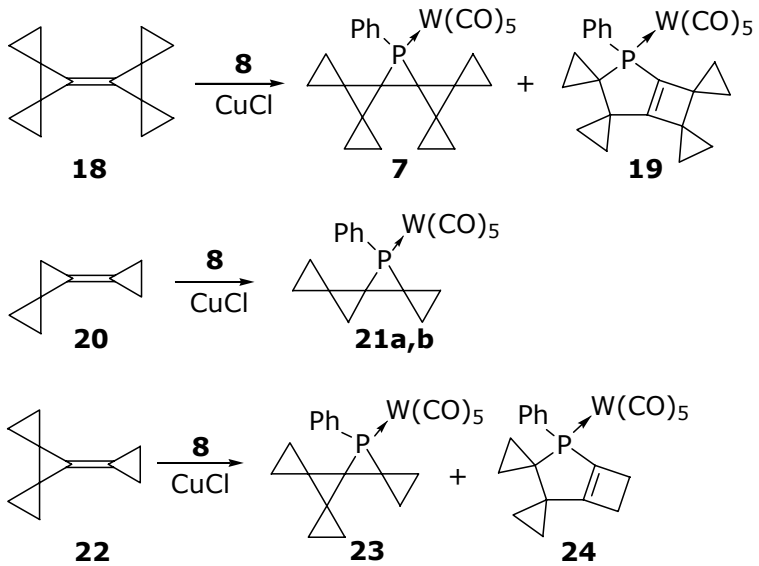


Figure 2. Displacement ellipsoid plot of **16b** (one of the two crystallographically independent molecules is shown) and **17a** in the crystal with ellipsoids set at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]; the values for the second molecule are in square brackets **16b**: C4-C5 1.422(12) [1.423(12)], C4-C7 1.500(13) [1.503(13)], C5-C6 1.289(14) [1.289(14)], C5-C7 1.456(14) [1.475(15)]; C1-P1-C2 48.4(4) [48.6(4)], C3-C1-C4 60.3(5) [60.5(5)], C5-C4-C7 59.7(6) [60.5(7)]. **17a**: C1-P1-C2 48.9(3), C6-P2-C7 48.9(3), C3-C1-C4 60.5(4), C4-C5-C6 58.2(4), C4-C6-C5 60.6(4).

The NMR characteristics of the phospha[*n*]triangulanes also reflect that their $W(CO)_5$-complexed phosphirane rings have similar electronic properties (Table 2). The phosphorus chemical shifts are in the narrow range of δ^{31}P –144 to –155 ppm with ^1J(P,W) coupling constants of 252–261 Hz. The less congested *anti* isomers are always formed predominantly[15] and have the more shielded ^{31}P NMR resonances,[16] which are similar to the δ –154.8 ppm reported for the parent 1-phenyl-phospha[2]triangulane complex **4b**.[5] The ^{13}C resonance of the phosphirane spiro-carbon C1 and carbon C2 are at δ 25–30 (**4b** 31.2) and δ 15–18 (**4b** 19.3) ppm, respectively. In addition, its two hydrogens resonate at about δ^1H 1.7 and 2.0 ppm with ^2J(H,P) coupling constants of < 1 and 7.1 Hz, respectively, with the larger one for the more deshielded proton resonance positioned *anti* to the P-$W(CO)_5$ group.

4.3 Spirocyclopropanated Bicyclopropylidenes

Alkenes with four alkyl substituents are more reactive toward electrophiles than terminal alkenes, because of their higher nucleophilicity, yet steric factors can hamper the access to the double bond. This is known for the addition of carbenes (*e.g.* MeCCl)[17] but is less clear for electrophilic phosphinidenes. Reactions of transient R-P=$W(CO)_5$ invariably have first-order kinetics for the uncatalyzed cheletropic elimination from phosphanorbornadiene precursor **8**.[18] Competition reactions showed no discrimination between simple substituted alkenes,[15] but the formation of the phosphaspiroalkanes **4b**-**e** from methylenecycloalkanes $H_2C=C(CH_2)_n$ occurs at different rates (n = 4 > 3 > 5 > 2) in the presence of CuCl.[5] The catalyst lowers the decomposition temperature for **8** from ca. 110 to 55 °C and can alter the kinetics of the alkene addition reaction.[19] Recently, a computational study addressed the role of the CuCl catalyst, showing (a) that the alkene may complex to it and (b) that the active reagent is likely [RP(Cl)$W(CO)_5$]-Cu-L, with L being the alkene or solvent.[20] In this section, the reactivity of spirocyclopropanated bicyclopropylidenes is first compared with that of the methylenecyclopropanes, while the influence of the CuCl catalyst is addressed in the next paragraph.



Scheme 3.

Bicyclopropylidene[21] is more reactive toward the CuCl-generated phosphinidene complex than both methylenecyclopropane[5] and 2,3-dimethyl-2-butene[15] and was shown to give the phospha[3]triangulane complex **5a**.[6] Adding a second sphere of spirocyclopropane rings gave the more electron-rich alkene **18**,[3] which still allows the formation of a phosphirane, yielding phospha[7]triangulane complex **7**,[11] as confirmed by an X-ray crystal structure determination (Figure 3). It was established that the yield of **7** decreases from 88 to 42% in the presence of CuCl with simultaneous formation of other products, like **19** (6%),[11] which may illustrate the influence of steric factors (Scheme 3). Therefore, the influence of the spirocyclopropane rings on the addition of the CuCl-generated phosphinidene complex to mono- and dispirocyclopropanated bicyclopropylidenes was examined (Scheme 3).

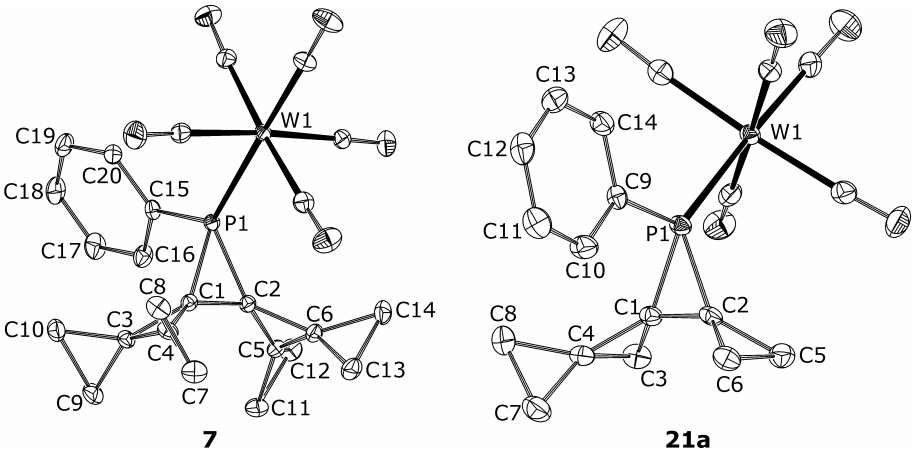


Figure 3. Displacement ellipsoid plot of **7** and **21a** with ellipsoids set at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] **7**: C3-C9 1.478(3), C3-C10 1.482(3), C4-C7 1.475(3), C4-C8 1.480(3), C5-C6 1.461(3), C5-C11 1.481(3), C5-12 1.483(3), C6-13 1.478(3), C6-C14 1.483(3), C7-C8 1.523(3), C9-C10 1.529(3), C11-C12 1.523(3), C13-C14 1.525(3); C3-C1-C4 59.02(13), C9-C3-C10 62.23(14), C7-C4-C8 62.07(15), C5-C2-C6 58.64(13), C11-C5-C12 61.83(15), C13-C6-C14 62.01(15); **21a**: C4-C7 1.487(4), C4-C8 1.473(4), C7-C8 1.521(4), C3-C1-C4 59.86(17), C5-C2-C6 61.10(18), C7-C4-C8 61.85(19).

Table 1. Selected X-ray crystallographic bond lengths for the phosphirane ring of terminal phospha[*n*]triangulanes.

	4b[4]	**12a**[a]		**14**	**16b**[a]		**17a**		Av.*
P1–C1	1.794(6)	1.799(2)	1.802(2)	1.801(2)	1.796(8)	1.792(8)	1.792(6)	1.792(6)	1.796
P1–C2	1.855(7)	1.846(3)	1.846(3)	1.836(2)	1.860(8)	1.850(8)	1.841(6)	1.846(6)	1.846
C1–C2	1.508(9)	1.495(4)	1.492(4)	1.490(3)	1.499(11)	1.501(11)	1.503(9)	1.507(9)	1.498
C1–C3	1.470(1)	1.504(4)	1.504(4)	1.486(3)	1.505(11)	1.494(11)	1.505(8)	1.505(8)	1.503[b]
C1–C4	1.475(10)	1.462(3)	1.467(3)	1.482(3)	1.468(11)	1.479(11)	1.469(9)	1.461(8)	1.468[b]
C3–C4	1.515(10)	1.480(4)	1.493(4)	1.461(3)	1.494(12)	1.497(11)	1.499(9)	1.497(9)	1.493[b]
P1–W1	2.500(2)	2.5107(7)	2.4980(7)	2.5063(5)	2.497(2)	2.497(2)	2.4822(16)	2.4733(16)	2.495

[a] Both crystallographically independent molecules are given. * Average of **12a**, **14**, **16b**, and **17a**. [b] Excluding **14** because of its symmetrical substituent pattern.

Table 2. Selected NMR parameters for the phosphirane ring of terminal phospha[*n*]triangulanes.

	12a		**12b**		**13b**		**13d**		**14**		**16b**		**16c**		**16d**		**17a**		**17b**	
^{31}P	–146.4		–152.3		–152.2		–154.9		–145.2		–144.0		–148.3		–148.5		–147.9		–150.4	–150.5
^{1}J(P,W)	257.2		254.1		258.1		255.5		252.1		258.2		257.2		256.2		261.2		260.2	258.2
^{13}C (C1)	26.5		25.7		26.7		25.6		29.6		29.0		29.1		28.3		26.3		25.6	26.1
^{1}J(C1,P)	6.1		7.1		6.7		8.6		10.1		7.7		7.5		9.3		8.8		9.8	5.5
^{13}C ($C2H_2$)	17.0		17.4		16.7		16.4		15.5		17.8		17.5		17.9		15.3		15.5	16.0
^{1}J(C2,P)	~6		6.1		6.3		6.4		5.7		5.8		6.1		6.0		6.3		6.1	6.3
^{1}H ($C2H_2$)	1.79	1.99	~1.6	2.02	~1.7	2.02	~1.7	1.88	1.62	2.09	1.83	2.02	1.70	2.13	1.65	2.05	1.59	2.24	1.75	2.28	~1.8	~1.8
^{2}J(H,P)	-	7.1	-	7.1	-	7.1	-	7.1	0.9	7.0	1.2	7.4	0.8	7.0	-	~7	-	7.1	-	6.9	unr.	unr.

Table 3. Selected X-ray crystallographic bond lengths for the phosphirane ring of phospha[*n*]triangulanes

	4a[4]	**5a**[5]	**7**	**21a**	**28a**[a]	**28a**[b]
P1–C1	1.80(2)	1.807(8)	1.8198(19)	1.821(2)	1.815(3)	1.834(3)
P1–C2	1.83(2)	1.820(8)	1.821(2)	1.816(2)	1.804(3)	1.823(3)
C1–C2	1.50(2)	1.48(1)	1.481(3)	1.470(3)	1.479(4)	1.526(4)
C1–C3		1.50(1)	1.487(3)	1.515(4)	1.490(3)	
C1–C4		1.51(1)	1.487(4)	1.468(3)	1.477(4)	
C2–C5		1.48(1)	1.494(3)	1.492(4)	1.484(4)	
C2–C6		1.49(1)	1.489(3)	1.489(4)	1.483(4)	
C3–C4		1.53(1)	1.465(3)	1.489(4)	1.505(4)	
C5–C6		1.51(1)	1.461(3)	1.515(4)	1.507(5)	
P1–W1	2.504(2)	2.495(2)	2.4872(5)	2.5120(7)	2.4817(7)	2.4876(7)
C1–P1–C2	48.6(7)	48.1(4)	47.99(8)	47.68(11)	48.25(12)	49.30(12)

[a] Disubstituted phosphirane ring. [b] Terminal phosphirane ring.

Table 4. Selected NMR parameters for the phosphirane ring of phospha[*n*]triangulanes.

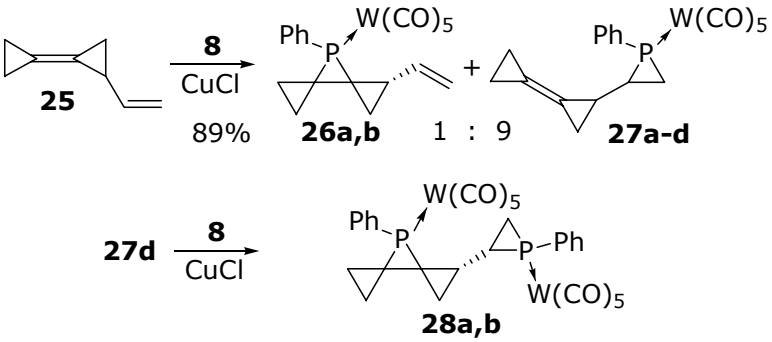
	4a[5]	**5a**[5]	**7**[11]	**21a**	**21b**	**23**	**26a**	**26b**	**28a**[a]	**28a**[b]	**28b**[a]	**28b**[b]
^{31}P	-187.6	-129.4	-119.6	-123.9	-128.1	-124.1	-127.0	-129.8	-127.1	-164.0	-129.6	-166.4
^{1}J(P,W)	257.5	251.6	250.1	257.2	254.1	250.6	259.4	260.4	258.7	252.6	259.7	251.6
^{13}C (C1/2)	10.7	26.0	34.5	30.1 24.8	30.0 25.3	32.3 23.5	31.0 26.5		31.8 25.1	27.4 16.0	31.4 25.9	27.3 15.8
^{1}J(C1/2,P)	12.2	27.7	6.2	2.3 -	3.5 -	5.7 -	2.2 -		3.8 -	16.2 11.6	5.3 -	15.9 11.4

[a] Disubstituted phosphirane ring. [b] Terminal phosphirane ring.

Reaction of **8** with cyclopropylidenespiropentane (**20**) in toluene at 55 °C in the presence of CuCl for one hour gave only the phospha[4]triangulane complex **21** (78%) in a 4:3 ratio of the fully characterized *anti* (**a**) and *syn* diastereomer (**b**). The structure of the less congested *anti* isomer **21a** was ascertained by an X-ray crystal structure determination (Figure 3). The bond lengths in the phosphirane ring compare well with the reported values of the smaller phospha[3]triangulane **5a**[6] (Table 3). The same reaction of **8** (RT, CuCl, 20 h) with 7-cyclopropylidenedispiro[2.0.2.1]heptane (**22**) afforded the branched phospha[5]-triangulane **23** (71%) and 2-phosphabicyclo[3.2.0]heptene **24** (2%) (Scheme 3). This reaction already takes place at room temperature, instead of the usual 55–60 °C,[12] indicating that the bicyclopropylidene with its tetrasubstituted double bond facilitates the CuCl-catalyzed reaction.[19,20] It is also evident that the second spirocyclopropane ring influences the phosphinidene addition, since **22** gave a small amount of byproduct that structurally resembles **19**. Before examining the influence of the catalyst, the special reactivity of the tetrasubstituted double bond in a bicyclopropylidene was compared with that of a vinyl substituent.

Reaction of **8** with an excess of ethenylbicyclopropylidene (**25**) in toluene at room temperature in the presence of CuCl gave after 18 h phospha[3]triangulane **26** (2 isomers: 1:1) and phosphirane **27** in 89% yield (4 isomers: 6:11:17:66) in a 1:9 ratio (Scheme 4). Both structure types were fully identified by NMR spectroscopy and show characteristic features, such as the ca. 40 ppm more shielded ^{31}P-NMR chemical shift for **27** that is common for the parent phosphiranes (*e.g.* major isomer *anti* **27d**: δ^{31}P = –169.5, *anti* **26a**: δ^{31}P = –127.0) (Table 4). Clearly, the [1+2]-cycloaddition of the phosphinidene complex to the single substituted and less sterically congested double bond is favored over that to the more electron-rich double bond in the bicyclopropylidene moiety, suggesting that steric factors do play a role. However, reaction of the isolated *anti* isomer **27d** with an excess of **8** at the higher temperature of 55 °C (CuCl, 6.5 h), did result in a second addition to give in 62% yield the phosphirane-substituted phospha[3]triangulane complex **28** in a 5:3 ratio of the *anti*,*anti* (**a**) and *anti,syn* isomer (**b**) (Scheme 4), with 12% recovery of the starting substrate **27d**. Isomer **28a** is easily recognized by its set of δ^{31}P NMR singlets (–127.1, ^{1}J(P,W) = 258.7 Hz; –164.0, ^{1}J(P,W) = 252.6 Hz) and isomer **28b** by its set of doublets (–129.6, ^{1}J(P,W) = 259.7 Hz; –166.4, ^{1}J(P,W) = 251.6 Hz; ^{4}J(P,P) = 4.1 Hz). The assignment of the *anti*,*anti*-isomer **28a** was confirmed by a

single-crystal X-ray structure, depicted in Figure 4, which shows a tightened cyclopropanated phosphirane ring[5,6] (P–C 1.810 (av); C1–C2 1.479(4)) as compared to the terminal one (P–C 1.829 (av); C1–C2 1.526(4)) (Table 3).



Scheme 4.

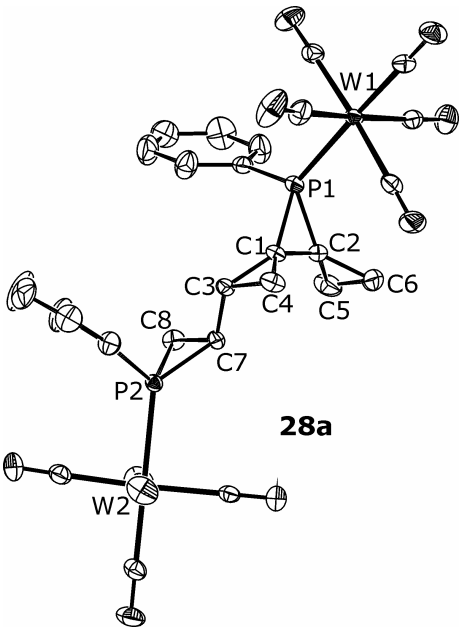
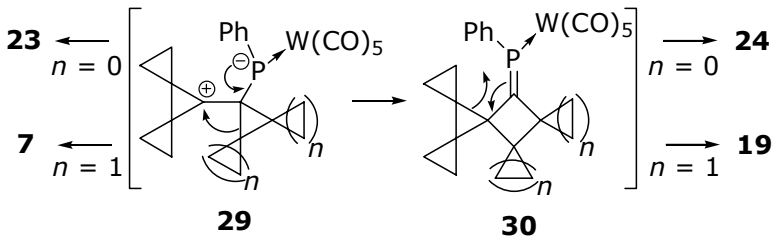


Figure 4. Displacement ellipsoid plot of **28a** with ellipsoids set at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C3-C7 1.487(4); C3-C1-C4 60.97(18), C5-C2-C6 61.1(2).

This phosphirane, with spirofused cyclopropanes at both carbons,[6] is similar to the PCC ring of **7** and **17a**. Selected X-ray crystal structural data for these phospha[*n*]triangulanes and the previously reported parent **4a**[5] and **5a**[6] are summarized in Table 3. Phospha[7]triangulane **7** has a P–C bond length of 1.820 Å (av.), which is comparable to the average length of the two unlike bonds (av. 1.796 and 1.846 Å) of the phospha[*n*]triangulanes with a terminal phosphirane ring (Table 1).

The additional spirofusion on the phosphirane ring is reflected in the NMR data (Tables 2 and 4) and most profoundly in the phosphorus chemical shift of δ^{31}P –120 to –130 ppm (^1J(P,W) = 250–260 Hz) that is deshielded by about 25 ppm compared to the terminal spirofused phosphirane complexes and by 55–65 ppm from that of the parent **4a** (δ –187.6 ppm).[5] The larger phospha[*n*]triangulanes ($n \geq 4$) have the slightly more deshielded ^{31}P NMR resonances, thereby showing only a modest influence of the second sphere of spirocyclopropane rings. This influence is also reflected in the ^{13}C NMR chemical shifts of δ 23.5–26.5 and 30.0–34.5 ppm for the spirofused phosphirane carbons with first and second sphere spirocyclopropane rings, respectively. The effect is the strongest for phospha[7]triangulane complex **7**[11] with δ^{13}C 34.5 ppm.



Scheme 5.

4.4 CuCl Catalysis

We return to the role of CuCl in the cycloaddition. Phosphiranes are the major products in all cases, suggesting that transient phosphinidene complex Ph-P=W(CO)$_5$ adds to the C=C bond. However, there are exceptions, namely alkenes **22** and **18** with their full second sphere of spirocyclopropane rings at one and both ends of the

double bond, respectively. They gave additional small amounts of the respective 2-phosphabicyclo[3.2.0]hept-1(5)-enes **19** and **24**. An X-ray crystal structure has been reported for **19**.[11] The NMR data of the two products are very similar. Characteristic are the ^{31}P and two ^{13}C chemical shifts for the ring C-P-C unit of **19** at δ^{31}P 34.4 (^1J(P,W) 238.4 Hz), δ^{13}C 34.9 (^1J(P,C) 39.7 Hz), and 142.5 ppm (^1J(P,C) 31.2 Hz)[11] and those for **24** at δ^{31}P 34.6 (^1J(P,W) 234.7 Hz), δ^{13}C 33.1 (^1J(P,C) 40.2 Hz), and 140.3 ppm (^1J(P,C) 29.7 Hz). These alkenes, **18** and **22**, but also **10** and **25**, differ from the others in the fact that they react at room temperature within 18–20 h with the phosphinidene precursor **8** instead of the 55–60 °C,[12] which is usually needed for the CuCl-catalyzed cycloadditions. Furthermore, the reactions executed at 55 °C occur rather fast (1–2 h) while the slower second cycloaddition for **16b** (3 h) and **27d** (6.5 h) differ from each other. These observations suggest that the elimination of the phosphinidene complex from the precursor is not necessarily the rate-limiting step, but that the alkene may be involved as well.[19] This notion concurs with a computational analysis,[20] which suggested that the alkene or aromatic solvent interacts with CuCl and that this complex dissociates the precursor to formally give [PhP(Cl)W(CO)$_5$]-Cu-L (L = alkene or solvent) as the active reagent. Phosphirane formation then occurs in an S_N2-type addition with a concurrent "chloride shuttle" back to the Cu ion to regenerate the CuCl-L complex. While the products for the uncatalyzed and CuCl-catalyzed reactions are usually the same, they can differ[22] and this was also the case with the alkenes **18** and **22**. Indeed, phosphatriangulane **7** was the sole product formed from **18** in the absence of CuCl.[11] There are two aspects, [PhP(Cl)W(CO)$_5$]-Cu-L is less reactive and bulkier than Ph-P=W(CO)$_5$ and thus more sensitive to steric constraints, which is the case here. We presume that the C=C bond interacts with the CuCl-L ligated phosphinidene complex under expulsion of the CuCl-L complex, forming zwitterion **29** (Scheme 5). Analogous σ-complexes were identified computationally to precede the formation of the 1,4-addition and C-H insertion products of azulenes.[23] Branched phospha[*n*]triangulanes **7** and **23** will result upon ring closure of the zwitterion, but steric factors may facilitate the well-known cyclopropylcarbinyl to cyclobutyl ring enlargement[24] to form phosphaalkene **30**. The ring expansion preferentially involves the more highly substituted cyclopropane ring, because in this manner the cationic charge can be delocalized best.[25,26] The reactive P=C bond of **30** enables a subsequent [1,3]-sigmatropic shift[27] that gives the 2-phosphabicyclo[3.2.0]heptenes **19** and **24**.

4.5 Conclusion

Novel, linear and branched mono- and diphospha[*n*]triangulanes have been synthesized in high yields by the CuCl-catalyzed phosphinidene addition to spiro-cyclopropanated methylenecyclopropanes and bicyclopropylidenes. Single crystal X-ray structure analyses of these remarkably stable products revealed a tightening of the phosphirane ring on spirocyclopropanation. The effect of spirofusion on the electronic properties of these strained phosphacycles is apparent from the NMR features that show deshielded chemical shifts for the phosphorus and carbon ring atoms. Steric factors play a role when the double bond carries a second sphere of spirocyclopropane rings and causes the formation of 2-phosphabicyclo-[3.2.0]heptenes as byproducts. The latter are explained to result from addition of the $[PhP(Cl)W(CO)_5]$-Cu-L (L = alkene or solvent) reagent to the spirocyclopropanated bicyclopropylidene to give an intermediate zwitterion, which can undergo a cyclopropylcarbinyl to cyclobutyl ring expansion followed by a [1,3]-sigmatropic shift.

4.6 Experimental Section

All experiments were performed under an atmosphere of dry nitrogen. Solids were dried in vacuo and liquids were distilled (under N_2) prior to use. Solvents were used as purchased, except for toluene, which was distilled over sodium. NMR spectra were recorded (at 298 K) on a Bruker Advance 250 (^{31}P; 85% H_3PO_4) and a MSL 400 (^1H, ^{13}C) and referenced internally to residual solvent resonances (^1H: δ 7.25 ppm ($CHCl_3$), $^{13}C\{^1H\}$: 77.0 ppm ($CDCl_3$). Isomeric ratios were determined by ^{31}P NMR spectroscopy. IR spectra were recorded on a Mattson-6030 Galaxy FT-IR spectrophotometer, and high-resolution mass spectra (HR-MS) were measured on a Finnigan Mat 900 mass spectrometer operating at an ionization potential of 70 eV. Melting points were measured on samples in unsealed capillaries and are uncorrected. CuCl (99% purity) was purchased from Acros and stored under nitrogen before use. (5,6-Dimethyl-2,3-bis(methoxycarbonyl)-7-phenyl-7-phosphanorbornadiene)pentacarbonyltungsten **8**,[9,13] methyl-enespiropentane (**9**),[28] 1-methylenedispiro[2.0.2.1]heptane (**10**),[29] 7-methylenedispiro-[2.0.2.1]heptane (**11**),[29,30] 1,4-bismethylenespiropentane (**15**),[31] perspiro-cyclopropanated bicyclopropylidene **18**,[3] cyclopropylidenespiropentane (**20**),[32] 7-cyclopropylidenedispiro-[2.0.2.1]heptane (**22**),[30] and ethenylbicyclopropylidene (**25**)[33] were prepared according to literature procedures.

(1-Phenyl-1-phosphadispiro[2.0.2.1]hept-1-yl)pentacarbonyltungsten (12): Complex **8** (360 mg, 0.55 mmol), methylenespiropentane (**9**) (132 mg, 1.65 mmol) and CuCl (10 mg, 0.1 mmol) were heated in toluene (4 mL) at 55 °C for 1 h. Evaporation to dryness and

chromatography of the residue over silica gel eluting with pentane/dichloromethane (19/1) gave **12a** and **b** in a 5:4 ratio (220 mg, 78%) as a pale yellow oil. Fractional crystallization from pentane at –80 °C followed by crystallization at –20 °C afforded colorless crystals of the *anti* isomer **12a**. ***Anti*-(1*R*,3*S*) and (1*S*,3*R*)-isomer 12a**: m.p. 64 °C; ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 0.49–0.55 (m, 1H; C*H*), 0.65–0.71 (m, 1H; C*H*), 0.85–0.91 (m, 1H; C*H*), 0.92–0.96 (m, 1H; C*H*), 1.39 (dd, ^{2}J(H,H) = 4.1 Hz, ^{3}J(H,P) = 6.2 Hz, 1H, PCC*H*), 1.77 (dd, ^{2}J(H,H) = 4.1 Hz, ^{3}J(H,P) = 10.2 Hz, 1H, PCC*H*), 1.79 (d, ^{2}J(H,H) = 7.6 Hz, 1H; PC*H*), 1.99 (dd, ^{2}J(H,H) = 7.6 Hz, ^{2}J(H,P) = 7.1 Hz, 1H; PC*H*), 7.30–7.38 (m, 5H; Ph*H*); ^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$): δ = 5.2 (d, ^{3}J(C,P) = 4.5 Hz; CH_2), 5.9 (s; CH_2), 17.0 (d, ^{1}J(C,P) = ~6 Hz; PCH_2), 17.1 (s; PCCH_2), 18.5 (d, ^{2}J(C,P) = 5.3 Hz; PC*C*), 26.5 (d, ^{1}J(C,P) = 6.1 Hz; P*C*), 128.6 (d, ^{3}J(C,P) = 10.5 Hz; *m*-Ph), 130.2 (d, ^{4}J(C,P) = 2.5 Hz; *p*-Ph), 131.4 (d, ^{2}J(C,P) = 13.4 Hz; *o*-Ph), 132.5 (d, ^{1}J(C,P) = 25.6 Hz; *ipso*-Ph), 195.6 (d, ^{2}J(C,P) = 8.4 Hz, ^{1}J(C,W) = 125.5 Hz; *cis*-CO), 197.9 (d, ^{2}J(C,P) = 30.0 Hz; *trans*-CO); ^{31}P NMR (101.25 MHz, $CDCl_3$): δ = – 146.4 (^{1}J(P,W) = 257.2 Hz); IR (KBr): ν = 1932 (s/br, CO_{eq}), 1983 (w, CO_{eq}), 2074 (w, CO_{ax}); MS (70 eV): *m/z* (%): 512 (8) $[M]^+$, 484 (4) $[M – CO]^+$, 456 (9) $[M – 2CO]^+$, 428 (8) $[M – 3CO]^+$, 400 (32) $[M – 4CO]^+$, 372 (100) $[M – 5CO]^+$; HR-MS (EI): calcd for $C_{17}H_{13}O_5P^{184}W$: 512.00104; found: 511.99819. ***Syn*-(1*R*,3*R*) and (1*S*,3*S*)-isomer 12b**: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 0.85–0.91 (m, 1H; C*H*), 0.91–0.97 (m, 1H; C*H*), 1.08–1.14 (m, 1H; C*H*), 1.20–1.25 (m, 1H; C*H*), 1.58–1.62 (m, 2H; PC*H*, PCC*H*), 1.68 (dd, ^{2}J(H,H) = 4.0 Hz, ^{3}J(H,P) = 11.1 Hz, 1H; PCC*H*), 2.02 (dd, ^{2}J(H,H) = 7.4 Hz, ^{2}J(H,P) = 7.1 Hz, 1H; PC*H*), 7.39–7.44 (m, 3H; *m*-Ph*H*, *p*-Ph*H*), 7.52–7.57 (m, 2H; *o*-Ph*H*); ^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$): δ = 5.2 (d, ^{3}J(C,P) = 1.8 Hz; CH_2), 6.2 (d, ^{3}J(C,P) = 3.4 Hz; CH_2), 16.4 (d, ^{2}J(C,P) = 3.5 Hz; PCCH_2), 17.4 (d, ^{1}J(C,P) = 6.1 Hz; PCH_2), 19.3 (s; PC*C*), 25.7 (d, ^{1}J(C,P) = 7.1 Hz; P*C*), 128.7 (d, ^{3}J(C,P) = 10.4 Hz; *m*-Ph), 130.2 (d, ^{4}J(C,P) = 2.3 Hz; *p*-Ph), 131.4 (d, ^{2}J(C,P) = 13.1 Hz; *o*-Ph), 134.6 (d, ^{1}J(C,P) = 25.4 Hz; *ipso*-Ph), 195.7 (d, ^{2}J(C,P) = 8.3 Hz, ^{1}J(C,W) = 125.6 Hz; *cis*-CO), 197.8 (d, ^{2}J(C,P) = 29.8 Hz; *trans*-CO); ^{31}P NMR (101.25 MHz, $CDCl_3$): δ = – 152.3 (^{1}J(P,W) = 254.1 Hz).

(1-Phenyl-1-phosphatrispiro[2.0.0.2.1.1]non-1-yl)pentacarbonyltungsten (13): Complex **8** (450 mg, 0.69 mmol), 1-methylenedispiro[2.0.2.1]heptane (**10**) (183 mg, 1.72 mmol), and CuCl (10 mg, 0.1 mmol) were stirred in toluene (4 mL) at room temperature for 18 hours. Evaporation to dryness and chromatography of the residue over silica gel eluting with pentane/dichloromethane (9/1) gave a 4:50:10:36 mixture of isomers **13a**, **b**, **c** and **d** (350 mg, 94 %) as a pale yellow oil. Crystallization from pentane at –80 °C afforded a 10:7 isomeric mixture of the main isomers **13b** and **13d**. **13a**: ^{31}P NMR (101.25 MHz, $CDCl_3$): δ = –147.3 (^{1}J(P,W) = 258.2 Hz). ***Anti*-(1*R*,3*S*,4*R*) and (1*S*,3*R*,4*S*)-isomer 13b**: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 0.76–0.96 (m, 5H; CH_2, PCCC*H*), 1.23–1.27 (m, 2H; PCC*H*, PCCC*H*), 1.68–1.73 (m, 1H; PC*H*), 1.81 (dd, ^{2}J(H,H) = 4.4 Hz, ^{3}J(H,P) = 10.0 Hz, 1H; PCC*H*), 2.02 (dd, ^{2}J(H,H) = 7.4 Hz, ^{2}J(H,P) = 7.1 Hz, 1H; PC*H*), 7.34–7.45 (m, 5H; Ph*H*); ^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$): δ = 4.0 (s; CH_2), 5.1 (d, ^{4}J(C,P) = 1.2 Hz; CH_2), 11.7 (d, ^{3}J(C,P) = 4.6 Hz; PCCC*H*), 14.7 (s;

PCC*C*), 16.1 (s; PCC*H*), 16.7 (d, ^{1}J(C,P) = 6.3 Hz; P*C*H$_2$), 22.4 (d, ^{2}J(C,P) = 8.8 Hz; PC*C*), 26.7 (d, ^{1}J(C,P) = 6.7 Hz; P*C*), 128.5 (d, ^{3}J(C,P) = 10.8 Hz; *m*-Ph), 130.3 (d, ^{4}J(C,P) = 2.7 Hz; *p*-Ph), 131.7 (d, ^{2}J(C,P) = 13.9 Hz; *o*-Ph), 132.0 (d, ^{1}J(C,P) = 24.9 Hz; *ipso*-Ph), 195.7 (d, ^{2}J(C,P) = 8.4 Hz, ^{1}J(C,W) = 125.5 Hz; *cis*-CO), 197.7 (d, ^{2}J(C,P) = 30.2 Hz; *trans*-CO); ^{31}P NMR (101.25 MHz, CDCl$_3$): δ = – 152.2 (^{1}J(P,W) = 258.1 Hz); MS (70 eV): (mixture of **13b** and **13d**): *m/z* (%): 538 (6) [*M*]$^+$, 482 (2) [*M* – 2CO]$^+$, 454 (5) [*M* – 3CO]$^+$, 426 (22) [*M* – 4CO]$^+$, 398 (88) [*M* – 5CO]$^+$; HR-MS (EI) calcd for $C_{19}H_{15}O_5P^{184}W$: 538.01672; found: 538.01741. **13c**: ^{31}P NMR (101.25 MHz, CDCl$_3$): δ = –152.3 (^{1}J(P,W) = 254.4 Hz). ***Syn*-(1*R*,3*R*,4*S*) and (1*S*,3*S*,4*R*)-isomer 13d**: ^{1}H NMR (400.13 MHz, CDCl$_3$): δ = 0.69–0.73 (m, 1H, C*H*), 0.76–0.96 (m, 3H; C*H*$_2$), 1.44 (dd, ^{2}J(H,H) = 4.3 Hz, ^{3}J(H,P) = 1.7 Hz, 1H; PCC*H*), 1.46, 1.47, 1.60, 1.61 (AB type, ^{2}J(H,H) = 4.3 Hz, 2H; PCCC*H*$_2$), 1.68–1.73 (m, 2H; PC*H*, PCC*H*), 1.88 (dd, ^{2}J(H,H) = 7.3 Hz, ^{2}J(H,P) = 7.1 Hz, 1H; PC*H*), 7.34–7.45 (m, 3H; *m*-Ph*H*, *p*-Ph*H*), 7.52–7.57 (m, 2H; *o*-Ph*H*); ^{13}C{^{1}H} NMR (100.62 MHz, CDCl$_3$): δ = 4.2 (s; C*H*$_2$), 4.8 (d, ^{4}J(C,P) = 2.1 Hz; C*H*$_2$), 12.7 (d, ^{3}J(C,P) = 3.9 Hz; PCCC*H*), 14.5 (d, ^{3}J(C,P) = 3.2 Hz; PCC*C*), 15.2 (d, ^{2}J(C,P) = 3.6 Hz; PC*C*H), 16.4 (d, ^{1}J(C,P) = 6.4 Hz; P*C*H$_2$), 23.1 (s; PC*C*), 25.6 (d, ^{1}J(C,P) = 8.6 Hz; P*C*), 128.7 (d, ^{3}J(C,P) = 10.4 Hz; *m*-Ph), 130.2 (d, ^{4}J(C,P) = 2.4 Hz; *p*-Ph), 131.5 (d, ^{2}J(C,P) = 13.1 Hz; *o*-Ph), 134.6 (d, ^{1}J(C,P) = 25.3 Hz; *ipso*-Ph), 195.7 (d, ^{2}J(C,P) = 8.3 Hz, ^{1}J(C,W) = 125.5 Hz; *cis*-CO), 197.9 (d, ^{2}J(C,P) = 30.0 Hz; *trans*-CO); ^{31}P NMR (101.25 MHz, CDCl$_3$): δ = –154.9 (^{1}J(P,W) = 255.5 Hz).

(1-Phenyl-1-phosphatrispiro[2.0.2.0.2.0]non-1-yl)pentacarbonyltungsten (14): Complex **8** (400 mg, 0.61 mmol), 7-methylenedispiro[2.0.2.1]heptane (**11**) (97 mg, 0.92 mmol) and CuCl (10 mg, 0.1 mmol) were heated in toluene (4 mL) at 55 °C for 1 h. Evaporation to dryness and chromatography of the residue over silica gel eluting with pentane/dichloromethane (9/1) gave **14** (290 mg, 88%) as a pale yellow oil. Crystallization from pentane at –20 °C afforded colorless crystals. **14**: m.p. 61–62 °C; ^{1}H NMR (400.13 MHz, CDCl$_3$): δ = 0.34–0.38 (m, 1H; C*H*), 0.57–0.62 (m, 1H; C*H*), 0.62–0.66 (m, 1H; C*H*), 0.70–0.73 (m, 1H; C*H*), 0.73–0.76 (m, 1H; C*H*), 0.88–0.95 (m, 2H; C*H*), 1.20–1.30 (m, 1H; C*H*), 1.62 (dd, ^{2}J(H,H) = 7.8 Hz, ^{2}J(H,P) = 0.9 Hz, 1H; PC*H*), 2.09 (dd, ^{2}J(H,H) = 7.8 Hz, ^{2}J(H,P) = 7.0 Hz, 1H; PC*H*), 7.36–7.48 (m, 5H; Ph*H*); ^{13}C{^{1}H} NMR (100.62 MHz, CDCl$_3$): δ = 4.4 (d, ^{3}J(C,P) = 3.8 Hz; *C*H$_2$), 4.7 and 5.0 (s; *C*H$_2$), 5.9 (d, ^{3}J(C,P) = 2.8 Hz; *C*H$_2$), 15.5 (d, ^{1}J(C,P) = 5.7 Hz; P*C*H$_2$), 22.5 (s; PC*C*), 22.5 (d, ^{2}J(C,P) = 5.7 Hz; PC*C*); 29.6 (d, ^{1}J(C,P) = 10.1 Hz; P*C*), 128.6 (d, ^{3}J(C,P) = 10.4 Hz; *m*-Ph), 130.2 (d, ^{4}J(C,P) = 2.3 Hz; *p*-Ph), 131.3 (d, ^{2}J(C,P) = 13.1 Hz; *o*-Ph), 132.9 (d, ^{1}J(C,P) = 25.9 Hz; *ipso*-Ph), 195.7 (d, ^{2}J(C,P) = 8.3 Hz, ^{1}J(C,W) = 125.5 Hz; *cis*-CO), 198.0 (d, ^{2}J(C,P) = 29.8 Hz; *trans*-CO); ^{31}P NMR (101.25 MHz, CDCl$_3$): δ = – 145.2 (^{1}J(P,W) = 252.1 Hz); IR (KBr): ν = 1917 (s/br, CO$_{eq}$), 1983 (w, CO$_{eq}$), 2070 (m, CO$_{ax}$); MS (70 eV): *m/z* (%): 538 (10) [*M*]$^+$, 482 (3) [*M* – 2CO]$^+$, 454 (16) [*M* – 3CO]$^+$, 426 (28) [*M* – 4CO]$^+$; HR-MS (EI): calcd for $C_{19}H_{15}O_5P^{184}W$: 538.01672; found: 538.01581; elemental analysis: calcd (%): C 42.41, H 2.81; found: C 41.68, H 2.89.

(1-Phenyl-1-phospha-5-methylenedispiro[2.0.2.1]hept-1-yl)pentacarbonyltungsten (16): Complex **8** (450 mg, 0.69 mmol), *rac*-1,4-dimethylenespiropentane (**15**) (191 mg, 2.07 mmol) and CuCl (10mg, 0.1 mmol) were heated in toluene (4 mL) at 55 °C for 2 h. Evaporation to dryness and chromatography of the residue over silica gel eluting with pentane/dichloromethane (19/1) gave a 12:39:31:18 mixture of isomers of **16a**,**b**,**c** and **d** (300 mg, 83%) as a pale yellow oil. **16b** could be separated by sequential column chromatography over silica gel eluting with pentane/dichloromethane (19/1). Colorless crystals were obtained from pentane at −20 °C. Those of **16c** could be isolated by fractional crystallization of the remaining mixture from pentane at −80 °C followed by crystallization at −20 °C. NMR data of the *syn* isomer **16d** could be obtained from the residual mixture of isomers. ***Syn*-(1*S*, 3*S*, 4*S*) and (1*R*,3*R*,4*R*)-isomer 16a**: ^{31}P NMR (101.25 MHz, $CDCl_3$): δ = −142.5 (^1J(P,W) = 257.8 Hz). ***Anti*-(1*R*,3*S*,4*R*) and (1*S*,3*R*,4*S*)-isomer 16b**: m.p. 47–48 °C; ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.08–1.11 (dddd, ^2J(H,H) = 8.4 Hz, ^4J(H,H) = 2.4 Hz, ^4J(H,H)= 1.8 Hz, ^4J(H,H) = 0.7 Hz, 1H; C*H*), 1.50 (ddd, ^2J(H,H)= 8.4 Hz, ^4J(H,H) = 2.4 Hz, ^4J(H,H) = 1.8 Hz, 1H; C*H*), 1.61 (ddd, ^2J(H,H)= 4.2 Hz, ^3J(H,P) = 6.8 Hz, ^4J(H,H) = 0.7 Hz, 1H; PCC*H*), 1.83 (dd, ^2J(H,H) = 7.7 Hz, ^2J(H,P) = 1.2 Hz, 1H; PC*H*), 2.02 (dd, ^2J(H,H) = 7.7 Hz, ^2J(H,P) = 7.4 Hz, 1H; PC*H*), 2.11 (dd, ^2J(H,H) = 4.2 Hz, ^3J(H,P) = 9.9 Hz, 1H; PCC*H*), 5.36 (t, ^4J(H,H) = 2.4 Hz, 1H; =C*H*), 5.39 (t, ^4J(H,H) = 1.8 Hz, 1H; =C*H*), 7.28–7.41 (m, 5H; Ph*H*); ^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$): δ = 9.5 (d, ^3J(C,P) = 4.6 Hz; *C*H$_2$), 17.8 (d, ^1J(C,P) = 5.8 Hz; P*C*H$_2$), 19.5 (s; PCCH$_2$), 19.5 (s; PCC), 29.0 (d, ^1J(C,P) = 7.7 Hz; P*C*), 101.6 (s; =CH$_2$), 128.6 (d, ^3J(C,P) = 10.9 Hz; *m*-Ph), 130.5 (d, ^4J(C,P) = 2.5 Hz; *p*-Ph), 131.3 (d, ^1J(C,P) = 25.8 Hz; *ipso*-Ph), 131.6 (d, ^2J(C,P) = 14.0 Hz; *o*-Ph), 133.7 (s; =*C*), 195.5 (d, ^2J(C,P) = 8.3 Hz, ^1J(C,W) = 125.5 Hz; *cis*-CO), 197.6 (d, ^2J(C,P) = 30.4 Hz; *trans*-CO); ^{31}P NMR (101.25 MHz, $CDCl_3$): δ = −144.0 (^1J(P,W) = 258.2 Hz); IR (KBr): ν = 1925 (s/br, CO_{eq}), 2074 (m, CO_{ax}); MS (70 eV): *m/z* (%): 524 (4) [*M*]$^+$, 468 (8) [*M* − 2CO]$^+$, 440 (3) [*M* − 3CO]$^+$, 412 (12) [*M* − 4CO]$^+$, 384 (52) [*M* − 5CO]$^+$; HR-MS (EI): calcd for $C_{18}H_{13}O_5P^{184}W$: 524.00104; found: 524.00082. ***Anti*-(1*R*,3*S*,4*S*) and (1*S*,3*R*,4*R*)-isomer 16c**: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.45–1.54 (m, 2H, C*H*), 1.70 (dd, ^2J(H,H) = 7.7 Hz, ^2J(H,P) = 0.8 Hz, 1H; PC*H*), 1.85 (dd, ^2J(H,H) = 4.2 Hz, ^3J(H,P) = 10.8 Hz, 1H; PCC*H*), 1.92 (dd, ^2J(H,H) = 4.2 Hz, ^3J(H,P) = 2.1 Hz, 1H; PCC*H*), 2.13 (dd, ^2J(H,H) = 7.7 Hz, ^2J(H,P) = 7.0 Hz, 1H; PC*H*), 5.51–5.53 (m, 2H; =C*H*$_2$), 7.40–7.45 (m, 3H; *m*-Ph*H*, *p*-Ph*H*), 7.51–7.57 (m, 2H; *o*-Ph*H*); ^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$): δ = 9.4 (d, ^3J(C,P) = 2.3 Hz; *C*H$_2$), 17.5 (d, ^1J(C,P) = 6.1 Hz; P*C*H$_2$), 19.3 (d, ^2J(C,P) = 3.5 Hz; PC*C*H$_2$), 20.5 (s; PC*C*), 29.1 (d, ^1J(C,P) = 7.5 Hz; P*C*), 102.7 (s; =*C*H$_2$), 128.8 (d, ^3J(C,P) = 10.5 Hz; *m*-Ph), 130.4 (d, ^4J(C,P) = 2.2 Hz; *p*-Ph), 131.4 (d, ^2J(C,P) = 13.3 Hz; *o*-Ph), 132.9 (d, ^3J(C,P) = 3.6 Hz; =*C*), 134.2 (d, ^1J(C,P) = 25.3 Hz; *ipso*-Ph), 195.6 (d, ^2J(C,P) = 8.4 Hz, ^1J(C,W) = 125.6 Hz; *cis*-CO), 197.7 (d, ^2J(C,P) = 30.7 Hz; *trans*-CO); ^{31}P NMR (101.25 MHz, $CDCl_3$): δ = −148.3 (^1J(P,W) = 257.2 Hz). ***Syn*-(1*S*,3*S*,4*R*) and (1*R*,3*R*,4*S*)-isomer 16d**: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.65 (d, ^2J(H,H) = 7.5 Hz, 1H; PC*H*), 1.71–1.74 (m, 1H; C*H*), 1.78–1.82 (m, 2H; PCC*H*, C*H*), 1.99–2.07 (m, 1H, ^3J(H,P) = 4.1 Hz, PCC*H*), 2.05 (d, ^2J(H,H) = 7.5 Hz, ^2J(H,P) = ~7 Hz, 1H; PC*H*), 5.29 (t, ^4J(H,H) = 2.4 Hz, 1H; =C*H*), 5.40 (t, ^4J(H,H) = 1.7 Hz, 1H; =C*H*), 7.41–7.45 (m, 3H; *m*-Ph*H*, *p*-Ph*H*), 7.52–7.58

(m, 2H; *o*-Ph*H*); $^{13}C\{^1H\}$ NMR (100.62 MHz, $CDCl_3$): δ = 10.5 (d, ^3J(C,P) = 4.3 Hz; *C*H_2), 17.9 (d, ^1J(C,P) = 6.0 Hz; P*C*H_2), 18.9 (d, ^2J(C,P) = 3.8 Hz; PC*C*H_2), 20.4 (s; PC*C*), 28.3 (d, ^1J(C,P) = 9.3 Hz; P*C*), 101.4 (d, ^4J(C,P) = 1.4 Hz; =*C*H_2), 128.8 (d, ^3J(C,P) = 10.4 Hz; *m*-Ph), 130.4 (d, ^4J(C,P) = 2.4 Hz; *p*-Ph), 131.3 (d, ^2J(C,P) = 13.0 Hz; *o*-Ph), 132.7 (d, ^3J(C,P) = 2.2 Hz; =*C*), 134.4 (d, ^1J(C,P) = 25.6 Hz; *ipso*-Ph), 195.5 (d, ^2J(C,P) = 8.3 Hz, ^1J(C,W) = 125.4 Hz; *cis*-CO), 197.6 (d, ^2J(C,P) = 30.4 Hz; *trans*-CO); ^{31}P NMR (101.25 MHz, $CDCl_3$): δ = –148.5 (^1J(P,W) = 256.2 Hz).

1,6-Di(pentacarbonyltungstino)-1,6-diphenyl-1,6-diphosphadispiro[2.0.0.2.1.1]nonane (17): 16b (88 mg, 0.17 mmol), complex **8** (219 mg, 0.33 mmol) and CuCl (10mg, 0.1 mmol) were heated in toluene (1 mL) at 55 °C for 3 h. Evaporation to dryness and chromatography of the residue over silica gel eluting with pentane/dichloromethane (9/1) gave **17a** and **b** in a 10:7 ratio (127 mg, 78%) as a colorless solid. Fractional crystallization from pentane/DCM at 0 °C afforded colorless crystals of **17a**. ***Anti,anti*-17a**: m.p. 198 °C (decomp.); ^1H NMR (400.13 MHz, $CDCl_3$): δ = 0.95 (dd, ^3J(H,P) = 6.5 Hz, ^2J(H,H) = 4.9 Hz, 2H; PCC*H*), 1.59 (d, ^2J(H,H) = 7.7 Hz, 2H; PC*H*), 1.76 (dd, ^3J(H,P) = 9.9 Hz, ^2J(H,H) = 4.9 Hz, 2H; PCC*H*), 2.24 (dd, ^2J(H,P) = 7.1 Hz, ^2J(H,H) = 7.7 Hz, 2H; PC*H*), 7.40–7.46 (m, 10H; Ph*H*); $^{13}C\{^1H\}$ NMR (100.62 MHz, $CDCl_3$): δ = 15.1 (m, $^{(2+3)}J$(C,P) = 4.6 Hz; PC*C*H), 15.3 (d, $^{(1+4)}J$(C,P) = 6.3 Hz; P*C*H_2), 25.4 (t, ^2J(C,P) = 5.5 Hz; PC*C*), 26.3 (d, $^{(1+3)}J$(C,P) = 8.8 Hz; P*C*), 128.8 (d, ^3J(C,P) = 10.8 Hz; *m*-Ph), 130.8 (m, ^4J(C,P) = 2.3 Hz; *p*-Ph), 131.4 (d, ^2J(C,P) = 13.9 Hz; *o*-Ph), 131.5 (d, ^1J(C,P) = 26.3 Hz; *ipso*-Ph), 195.3 (d, ^2J(C,P) = 8.4 Hz, ^1J(C,W) = 125.4 Hz; *cis*-CO), 197.3 (d, ^2J(C,P) = 31.1 Hz; *trans*-CO); ^{31}P NMR (101.25 MHz, $CDCl_3$): δ = –147.9 (^1J(P,W) = 261.2 Hz); IR (KBr): ν = 1917 and 1935 (s/br, CO_{eq}), 1991 (w, CO_{eq}), 2074 (m, CO_{ax}); MS (70 eV): *m/z* (%): 956 (8) $[M]^+$, 900 (1) $[M - 2CO]^+$, 844 (16) $[M - 4CO]^+$, 788 (20) $[M - 6CO]^+$, 732 (40) $[M - 8CO]^+$, 676 (100) $[M - 10CO]^+$; HR-MS (EI): calcd for $C_{29}H_{18}O_{10}P_2{}^{184}W_2$: 955.93945, found: 955.93875; elemental analysis: calcd (%): C 36.43, H 1.90; found: C 36.12, H 1.95. ***Anti,syn*-17b**: ^1H NMR (400.13 MHz, $CDCl_3$): δ = 1.05 (dd, ^3J(H,P) = 1.5 Hz, ^2J(H,H) = 4.6 Hz, 1H; PCC*H*), 1.58 (dd, ^3J(H,P) = 10.8 Hz, ^2J(H,H) = 4.7 Hz, 1H; PCC*H*), 1.75 (d, ^2J(H,H) = 8.1 Hz, 1H; PC*H*), 1.80 (dd, ^3J(H,P) = 6.5 Hz, ^2J(H,H) = 5.0 Hz, 1H; PCC*H*), 1.81–1.87 (m, 2H; PC*H*), 2.00 (dd, ^3J(H,P) = 9.6 Hz, ^2J(H,H) = 5.0 Hz, 1H; PCC*H*), 2.28 (dd, ^2J(H,P) = 6.9 Hz, ^2J(H,H) = 8.2 Hz, 1H; PC*H*), 7.38–7.48 (m, 10H; Ph*H*); $^{13}C\{^1H\}$ NMR (100.62 MHz, $CDCl_3$): δ = 14.2 (dd, ^2J(C,P) = 3.9 Hz; PC*C*H), 15.5 (d, ^1J(C,P) = 6.1 Hz; P*C*H_2), 16.0 (d, ^1J(C,P) = 6.3 Hz; P*C*H_2), 16.1 (d, ^2J(C,P) = 3.1 Hz; PC*C*H), 25.6 (d, ^1J(C,P) = 9.8 Hz; P*C*), 26.1 (d, ^1J(C,P) = 5.5 Hz; P*C*), 26.4 (dd, ^2J(C,P) = 2.1 Hz, ^2J(C,P) = 8.9 Hz; PC*C*), 128.7 (d, ^3J(C,P) = 10.5 Hz; *m*-Ph), 128.9 (d, ^3J(C,P) = 10.4 Hz; *m*-Ph), 130.5 (d, ^4J(C,P) = 2.3 Hz; *p*-Ph), 130.6 (d, ^4J(C,P) = 2.4 Hz; *p*-Ph), 131.2 (d, ^2J(C,P) = 13.0 Hz; *o*-Ph), 131.4 (d, ^2J(C,P) = 13.4 Hz; *o*-Ph), 131.7 (d, ^1J(C,P) = 25.4 Hz; *ipso*-Ph), 133.8 (d, ^1J(C,P) = 26.1 Hz; *ipso*-Ph), 195.3 (d, ^2J(C,P) = 8.1 Hz, ^1J(C,W) = 125.4 Hz; *cis*-CO), 195.5 (d, ^2J(C,P) = 8.0 Hz, ^1J(C,W) = 125.4 Hz; *cis*-CO), 197.3 (d, ^2J(C,P) = 30.4 Hz; *trans*-CO), 197.4 (d, ^2J(C,P) = 30.6 Hz; *trans*-CO); ^{31}P NMR (101.25 MHz, $CDCl_3$):

δ = –150.4 (^1J(P,W) = 260.2 Hz, ^4J(P,P) = 5.1 Hz), –150.5 (^1J(P,W) = 258.2 Hz, ^4J(P,P) = 4.1 Hz).

Synthesis of 7 and 19: Complex **8** (0.65 g, 1.00 mmol), perspirocyclopropanated bicyclopropylidene **18** (0.22 g, 1.20 mmol) and CuCl (10 mg, 0.1 mmol) were stirred at room temperature for 20 h in toluene (4 mL). Evaporation to dryness and chromatography of the residue over silica gel eluting with pentane/dichloromethane (19/1) yielded both **7** (0.26 g, 42%) and **19** (40 mg, 6%) as pale yellow solids. Crystallization of **7** from hexane at –20 °C and **19** from diethyl ether at – 5 °C afforded colorless crystals for both.

(15-Phenyl-15-phosphahexaspiro[2.0.2.0.0.0.2.0.2.0.1]pentadec-15-yl)pentacarbonyltungsten (7): m.p. 178–179 °C (decomp); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.60–0.68 (m, 4H; CH_2), 0.75–0.80 (m, 2H; CH_2), 0.85–0.96 (m, 6H; CH_2), 0.96–1.02 (m, 2H; CH_2), 1.22–1.28 (m, 2H; CH_2), 7.25–7.39 (m, 5H; Ph*H*); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ = 4.4 (d, ^3J(C,P) = 4.0 Hz; *C*H$_2$), 4.7 (d, ^3J(C,P) = 3.3 Hz; *C*H$_2$), 7.1 (d, ^3J(C,P) = 2.1 Hz; *C*H$_2$), 7.4 (s; *C*H$_2$), 21.8 (d, ^2J(C,P) = 5.3 Hz; PC*C*), 21.9 (d, ^2J(C,P) = 1.2 Hz; PC*C*), 34.5 (d, ^1J(C,P) = 6.2 Hz; P*C*), 128.2 (d, ^3J(C,P) = 10.2 Hz; *m*-Ph), 130.0 (d, ^4J(C,P) = 2.6 Hz; *p*-Ph), 131.9 (d, ^2J(C,P) = 13.1 Hz; *o*-Ph), 132.9 (d, ^1J(C,P) = 19.9 Hz; *ipso*-Ph), 195.9 (d, ^2J(C,P) = 8.3, ^1J(C,W) = 125.4 Hz; *cis*-CO), 198.9 (d, ^2J(C,P) = 29.5 Hz; *trans*-CO); ^{31}P{^{1}H} NMR (101.3 MHz, $CDCl_3$): δ = –119.6 (^1J(P,W) = 250.1 Hz); IR (KBr): ν = 1923, 1942 (s/br, CO_{eq}), 1985 (w, CO_{eq}), 2072 cm^{-1} (m, CO_{ax}); MS (70 eV): *m/z* (%): 616 (4) [*M*]$^+$; HR-MS (EI, 70 eV): calcd for $C_{25}H_{21}O_5P^{184}W$: 616.06366, found: 616.06655.

{2-Phenyl-2-phospha-3:3,4:4,6:6,7:7-tetrakisethanobicyclo[3.2.0]hept-1(5)-en-2-yl}-pentacarbonyltungsten (19): m.p. 146–148 °C; ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.23–0.29 (m, 1H; CH_2), 0.33–0.42 (m, 2H; CH_2), 0.51–0.59 (m, 2H; CH_2), 0.61–0.71 (m, 6H; CH_2), 0.79–0.83 (m, 2H, CH_2) 0.91–0.98 (m, 2H; CH_2), 1.10–1.14 (m, 1H, CH_2), 7.40–7.44 (m, 3H; *m*-Ph*H*, *p*-Ph*H*), 7.50–7.56 (m, 2H; *o*-Ph*H*); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ = 6.3, 6.6, 7.7, 7.8, 7.9, 8.8 (s; *C*H$_2$), 10.1 (d, ^2J(C,P) = 2.9 Hz; PC*C*H$_2$), 10.4 (d, ^2J(C,P) = 7.1 Hz; PC*C*H$_2$), 30.6 (d, ^2J(C,P) = 7.7 Hz; PC*C*), 34.9 (d, ^1J(C,P) = 39.7 Hz; P*C*), 35.2 (d, ^2J(C,P) = 22.1 Hz; P(C=)*C*), 35.8 (d, ^3J(C,P) = 4.2 Hz; PC=C*C*), 128.5 (d, ^3J(C,P) = 9.6 Hz; *m*-Ph), 130.3 (d, ^4J(C,P) = 2.1 Hz; *p*-Ph), 131.4 (d, ^2J(C,P) = 12.3 Hz; *o*-Ph), 136.3 (d, ^1J(C,P) = 32.5 Hz; *ipso*-Ph), 142.5 (d, ^1J(C,P) = 31.2 Hz; P*C*=C), 172.0 (d, ^2J(C,P) = 5.8 Hz; PC=*C*), 196.8 (d, ^2J(C,P) = 7.1, ^1J(C,W) = 125.4 Hz; *cis*-CO), 199.3 (d, ^2J(C,P) = 21.1 Hz; *trans*-CO); ^{31}P{^{1}H} NMR (101.3 MHz, $CDCl_3$): δ = 34.4 (^1J(P,W) = 238.4 Hz); IR (KBr): ν = 1908, 1933 (s/br, CO_{eq}), 1977 (w, CO_{eq}), 2068 cm^{-1} (m, CO_{ax}); MS (70 eV): *m/z* (%): 616 (2) [*M*]$^+$; HR-MS (EI, 70 eV): calcd for $C_{25}H_{21}O_5P^{184}W$: 616.06366, found: 616.06445.

(8-Phenyl-8-phosphatrispiro[2.0.0.2.1.1]non-8-yl)pentacarbonyltungsten (21): Complex **8** (369 mg, 0.55 mmol), cyclopropylidenespiropentane (**20**) (117 mg, 1.10 mmol) and CuCl (10mg, 0.1 mmol) were heated in toluene (4 mL) at 55 °C for 1 h. Evaporation to dryness and

chromatography of the residue over silica gel eluting with pentane/dichloromethane (19/1) gave **21a** and **b** in a 4:3 ratio (220 mg, 78%) as a pale yellow oil. Fractional crystallization from pentane at –20 °C afforded colorless crystals of both isomers. ***Anti*-(4*R*,9*R*) and (4*S*,9*S*)-Isomer 21a**: m.p. 99 °C; ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 0.43–0.48 (m, 1H; C*H*), 0.76–0.91 (m, 3H; C*H*), 0.93–1.00 (m, 1H; PCC*H*), 1.13 (dd, ^{2}J(H,H) = 4.3 Hz, ^{2}J(H,P) = 7.0 Hz, 1H, PCC*H*C), 1.35–1.46 (m, 2H; PCC*H*), 1.47–1.53 (m, 1H; PCC*H*), 1.67 (dd, ^{2}J(H,H) = 4.3 Hz, ^{2}J(H,P) = 10.9 Hz, 1H; PCC*H*C), 7.35–7.46 (m, 5H; Ph*H*); ^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$): δ = 3.9 (d, ^{3}J(C,P) = 4.6 Hz; *C*H_2), 4.7 (s; *C*H_2), 7.4 (d, ^{2}J(C,P) = 3.6 Hz; PC*C*H_2), 8.9 (s; PC*C*H_2), 15.0 (s; PC*C*H_2C), 18.0 (d, ^{2}J(C,P) = 5.3 Hz; PC*C*), 24.8 (s; P*C*), 30.1 (d, ^{1}J(C,P) = 2.3 Hz; P*C*), 128.4 (d, ^{3}J(C,P) = 10.5 Hz; *m*-Ph), 130.2 (d, ^{4}J(C,P) = 2.6 Hz; *p*-Ph), 132.2 (d, ^{2}J(C,P) = 13.5 Hz; *o*-Ph), 132.6 (d, ^{1}J(C,P) = 21.5 Hz; *ipso*-Ph), 195.6 (d, ^{2}J(C,P) = 8.4 Hz, ^{1}J(C,W) = 125.4 Hz; *cis*-CO), 197.8 (d, ^{2}J(C,P) = 29.4 Hz; *trans*-CO); ^{31}P NMR (101.25 MHz, $CDCl_3$): δ = –123.9 (^{1}J(P,W) = 257.2 Hz); IR (KBr): ν = 1914 and 1931 (s/br, CO_{eq}), 1987 (w, CO_{eq}), 2072 (m, CO_{ax}); MS (70 eV): *m/z* (%): 538 (2) [*M*]$^{+}$, 454 (3) [*M* – 3CO]$^{+}$, 426 (6) [*M* – 4CO]$^{+}$, 398 (20) [*M* – 5CO]$^{+}$; HR-MS (EI): calcd for $C_{19}H_{15}O_5P^{184}W$: 538.01672, found: 538.01570; elemental analysis: calcd (%): C 42.41, H 2.81; found: C 42.24, H 2.82. ***Syn*-(4*S*,9*R*) and (4*R*,9*S*)-isomer 21b**: m.p. 74–75 °C; ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 0.77–0.84 (m, 1H; C*H*), 0.95–1.07 (m, 2H; C*H*), 1.10–1.20 (m, 2H; C*H*, PCC*H*), 1.22–1.30 (m, 2H; PCC*H*), 1.32 (dd, ^{2}J(H,H) = 4.2 Hz, ^{2}J(H,P) = 2.6 Hz, 1H; PCC*H*C), 1.34–1.44 (m, 1H; PCC*H*), 1.51 (dd, ^{2}J(H,H) = 4.2 Hz, ^{2}J(H,P) = 11.9 Hz, 1H; PCC*H*C), 7.38–7.46 (m, 3H; *m*-Ph*H*, *p*-Ph*H*), 7.56–7.64 (m, 2H; *o*-Ph*H*); ^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$): δ = 4.1 (d, ^{3}J(C,P) = 2.4 Hz; *C*H_2), 5.2 (d, ^{3}J(C,P) = 3.7 Hz; *C*H_2), 8.0 (d, ^{2}J(C,P) = 3.5 Hz; PC*C*H_2), 8.2 (s; PC*C*H_2), 14.9 (d, ^{2}J(C,P) = 3.8 Hz; PC*C*H_2C), 18.8 (s; PC*C*), 25.3 (s; P*C*), 30.0 (d, ^{1}J(C,P) = 3.5 Hz; P*C*), 128.5 (d, ^{3}J(C,P) = 10.5 Hz; *m*-Ph), 130.2 (d, ^{4}J(C,P) = 2.6 Hz; *p*-Ph), 132.3 (d, ^{2}J(C,P) = 13.4 Hz; *o*-Ph), 134.0 (d, ^{1}J(C,P) = 20.7 Hz; *ipso*-Ph), 195.7 (d, ^{2}J(C,P) = 8.3 Hz, ^{1}J(C,W) = 125.4 Hz; *cis*-CO), 197.7 (d, ^{2}J(C,P) = 29.4 Hz; *trans*-CO); ^{31}P NMR (101.25 MHz, $CDCl_3$): δ = –128.1 (^{1}J(P,W) = 254.1 Hz); IR (KBr): ν = 1937 (s/br, CO_{eq}), 1987 (w, CO_{eq}), 2072 (w, CO_{ax}).

Synthesis of 23 and 24: Complex **8** (0.33 g, 0.50 mmol), 7-cyclopropylidenedispiro-[2.0.2.1]heptane (**22**) (0.13 g, 1.00 mmol) and CuCl (10 mg, 0.1 mmol) were stirred at room temperature for 20 h in toluene (4 mL). Evaporation to dryness and chromatography of the residue over silica gel eluting with pentane/dichloromethane (9/1) yielded **23** and **24** as a pale yellow solid. Fractional crystallization from pentane at 0 °C afforded colorless crystals of **23** (200 mg, 71%). **24** was obtained as a colorless oil (5 mg, 2%) after sequential column chromatography over silica gel eluting with pentane/dichloromethane (9/1).

(11-Phenyl-11-phosphatetraspiro[2.0.2.0.0.2.1]undec-11-yl)pentacarbonyltungsten (23): m.p. 93 °C; ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 0.19–0.24 (m, 1H; C*H*), 0.49–0.57 (m, 1H; C*H*), 0.58–0.64 (m, 2H; C*H*), 0.76–0.86 (m, 2H; C*H*), 0.96–1.02 (m, 1H; C*H*), 1.10–1.27 (m, 3H; C*H*, PCCH_2), 1.47–1.61 (m, 2H; PCCH_2), 7.35–7.40 (m, 3H; *m*-Ph*H*, *p*-Ph*H*), 7.48–7.54 (m,

2H; *o*-Ph*H*); $^{13}C\{^1H\}$ NMR (100.62 MHz, $CDCl_3$): δ = 3.0 (d, ^3J(C,P) = 4.0 Hz; *C*H_2), 3.5 (d, ^3J(C,P) = 1.6 Hz; *C*H_2), 3.9 (s; *C*H_2), 4.6 (d, ^3J(C,P) = 3.2 Hz; *C*H_2), 6.8 (s; PC*C*H_2), 6.9 (d, ^2J(C,P) = 3.3 Hz; PC*C*H_2), 20.8 (d, ^2J(C,P) = 1.7 Hz; PC*C*), 21.5 (d, ^2J(C,P) = 5.6 Hz; PC*C*), 23.5 (s; P*C*$(CH_2)_2$), 32.2 (d, ^1J(C,P) = 5.7 Hz; P*C*), 128.4 (d, ^3J(C,P) = 10.5 Hz; *m*-Ph), 130.2 (d, ^4J(C,P) = 2.6 Hz; *p*-Ph), 132.0 (d, ^2J(C,P) = 13.2 Hz; *o*-Ph), 133.1 (d, ^1J(C,P) = 21.0 Hz; *ipso*-Ph), 195.7 (d, ^2J(C,P) = 8.4 Hz, ^1J(C,W) = 125.5 Hz; *cis*-CO), 197.9 (d, ^2J(C,P) = 29.4 Hz, ^1J(C,W) = 149.6 Hz; *trans*-CO); ^{31}P NMR (101.25 MHz, $CDCl_3$): δ = –124.1 (^1J(P,W) = 250.6 Hz); IR (KBr): ν = 1915, 1933 (s/br, CO_{eq}), 1979 (m, CO_{eq}), 2072 cm^{-1} (m, CO_{ax}); MS (70 eV): *m/z* (%): 564 (13) $[M]^+$, 508 (2) $[M - 2CO]^+$, 480 (7) $[M - 3CO]^+$, 452 (19) $[M - 4CO]^+$, 424 (100) $[M - 5CO]^+$; HR-MS (EI): calcd for $C_{21}H_{17}O_5P^{184}W$: 564.03235, found: 564.03512.

{2-Phenyl-2-phospha-3:3,4:4-bisethanobicyclo[3.2.0]hept-1(5)-en-2-yl}pentacarbonyltungsten (24): ^1H NMR (400.1 MHz, $CDCl_3$): δ = 0.21–0.31 (m, 2H; PCCC*H*, PCC*H*), 0.32–0.40 (m, 1H; PCC*H*), 0.49–0.55 (m, 1H; PCC*H*), 0.62–0.74 (m, 3H; PCCC*H*), 0.90–0.99 (m, 1H, PCC*H*), 2.79–2.91 (m, 2H; =CC*H*), 2.96–3.12 (m, 2H, =CC*H*), 7.40–7.51 (m, 5H; Ph*H*); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 7.7, 8.9 (s; PCC*C*H_2), 10.8 (d, ^2J(C,P) = 3.1 Hz; PC*C*H_2), 11.1 (d, ^2J(C,P) = 7.4 Hz; PC*C*H_2), 28.5 (d, ^2J(C,P) = 2.5 Hz; P(C=)*C*H_2), 28.7 (d, ^3J(C,P) = 15.8 Hz; PC=C*C*H_2), 31.4 (d, ^2J(C,P) = 8.2 Hz; PC*C*), 33.1 (d, ^1J(C,P) = 40.2 Hz; P*C*), 128.6 (d, ^3J(C,P) = 9.6 Hz; *m*-Ph), 130.4 (d, ^4J(C,P) = 2.1 Hz; *p*-Ph), 131.6 (d, ^2J(C,P) = 12.2 Hz; *o*-Ph), 136.0 (d, ^1J(C,P) = 32.3 Hz; *ipso*-Ph), 140.3 (d, ^1J(C,P) = 29.7 Hz; P*C*=C), 170.6 (d, ^2J(C,P) = 4.4 Hz; PC=*C*), 196.7 (d, ^2J(C,P) = 7.1, ^1J(C,W) = 125.4 Hz; *cis*-CO), 199.5 (d, ^2J(C,P) = 21.0 Hz; *trans*-CO); ^{31}P NMR (101.25 MHz, $CDCl_3$): δ = 34.6 ($^1J_{P,W}$ = 234.7 Hz); MS (70 eV): *m/z* (%): 564 (10) $[M]^+$, 508 (2) $[M - 2CO]^+$, 480 (5) $[M - 3CO]^+$, 452 (4) $[M - 4CO]^+$, 424 (20) $[M - 5CO]^+$; HR-MS (EI): calcd for $C_{21}H_{17}O_5P^{184}W$: 564.03235, found: 564.03554.

Synthesis of 26 and 27: Complex **8** (600 mg, 0.92 mmol), ethenylbicyclopropylidene (**25**) (293 mg, 2.76 mmol) and CuCl (10mg, 0.1 mmol) were stirred in toluene (4 mL) at room temperature for 18 h. Evaporation to dryness and chromatography of the residue over silica gel eluting with pentane/dichloromethane (19/1) gave a mixture of 6 phosphirane isomers (440 mg, 89%) as a pale yellow oil. This mixture consisted of 9% of the phospha[3]triangulane isomers **26a** and **b** (1:1 ratio) and 91% of the phosphiranes **27** (4 isomers, 6:11:17:66). Colorless crystals of **27d** could be isolated by fractional crystallization from hexane at –80 °C followed by recrystallization at –80 °C. **26a** could be separated from the remaining isomers by subsequent column chromatography over silica gel eluting with pentane/dichloromethane (19/1) and crystallization at –80 °C.

(1-Ethenyl-7-phenyl-7-phosphadispiro[2.0.2.1]hept-7-yl)pentacarbonyltungsten (26). *Anti*-(1*R*,3*S*,7*S*)- and (1*S*,3*R*,7*R*)-isomer 26a: ^1H NMR (400.13 MHz, $CDCl_3$): δ = 0.90–1.02 (m, 1H; C*H*), 1.02–1.08 (m, ^2J(H,H) = 5.3 Hz, 1H; C*H*), 1.15–1.25 (m, 1H; C*H*), 1.40–1.50 (m, 1H; C*H*), 1.50–1.61 (m, 1H; C*H*), 1.74–1.81 (m, ^2J(H,H) = 5.3 Hz, 1H; C*H*), 2.37–2.43 (m, 1H; PCC*H*), 5.08–5.11 (m, 1H; =CH_2), 5.24–5.28 (m, 2H; =CH_2, =C*H*), 7.42–7.46 (m, 3H; *m*-Ph*H*,

p-Ph*H*), 7.56–7.62 (m, 2H; *o*-Ph*H*); $^{13}C\{^1H\}$ NMR (100.62 MHz, $CDCl_3$): δ = 7.6 (d, ^2J(C,P) = 3.4 Hz; *C*H_2), 9.8 (s; *C*H_2), 17.3 (s; *C*H_2), 26.5 (s; P*C*), 27.1 (d, ^2J(C,P) = 3.1 Hz; PC*C*H), 31.0 (d, ^1J(C,P) = 2.2 Hz; P*C*), 115.9 (s; =*C*H_2), 128.5 (d, ^3J(C,P) = 10.9 Hz; *m*-Ph), 130.4 (d, ^4J(C,P) = 2.7 Hz; *p*-Ph), 132.7 (d, ^1J(C,P) = 21.6 Hz; *ipso*-Ph), 133.1 (d, ^2J(C,P) = 14.2 Hz; *o*-Ph), 137.6 (s; =*C*H), 195.5 (d, ^2J(C,P) = 8.3 Hz; *cis*-CO), 197.5 (d, ^2J(C,P) = 29.5 Hz; *trans*-CO); ^{31}P NMR (101.25 MHz, $CDCl_3$): δ = −127.0 (^1J(P,W) = 259.4 Hz). ***Syn*-(1*R*,3*S*,7*R*) and (1*S*,3*R*,7*S*)-isomer 26b**: ^{31}P NMR (101.25 MHz, $CDCl_3$): δ = −129.8 (^1J(P,W) = 260.4 Hz).

(1-Phenyl-2-bicyclopropylidenylphosphiranyl)pentacarbonyltungsten (27). 27a: ^{31}P NMR (101.25 MHz, $CDCl_3$): δ = −165.7 (^1J(P,W) = 257.8 Hz). **27b**: ^{31}P NMR (101.25 MHz, $CDCl_3$): δ = −167.7 (^1J(P,W) = 258.0 Hz). **27c**: ^{31}P NMR (101.25 MHz, $CDCl_3$): δ = −167.7 (^1J(P,W) = 252.8 Hz). ***Anti*-(1*S*,2*S*,4*R*) and (1*R*,2*R*,4*S*)-isomer 27d**: m.p. 61 °C; ^1H NMR (400.13 MHz, $CDCl_3$): δ = 0.73–0.81 (m, 2H; =CC*H*), 1.01–1.13 (m, 2H; =CC*H*), 1.13–1.20 (m, 1H; PCCCH_2), 1.32–1.37 (m, 1H; PCC*H*), 1.40–1.46 (m, 1H; PCCCH_2), 1.52–1.58 (m, 1H; P*C*H_2), 1.64–1.70 (m, 1H; P*C*H), 1.70–1.76 (m, 1H; P*C*H_2), 7.35–7.42 (m, 3H; *m*-Ph*H*, *p*-Ph*H*), 7.50–7.62 (m, 2H; *o*-Ph*H*); $^{13}C\{^1H\}$ NMR (100.62 MHz, $CDCl_3$): δ = 2.8 and 3.0 (s; =C(*C*$H_2)_2$), 10.4 (d, ^3J(C,P) = 5.0 Hz; PCC*C*H_2), 14.7 (d, ^1J(C,P) = 11.8 Hz; P*C*H_2), 16.3 (d, ^2J(C,P) = 4.0 Hz; PC*C*H), 28.5 (d, ^1J(C,P) = 16.3 Hz; P*C*H), 112.9 (s; =*C*$(CH_2)_2$), 113.3 (d, ^3J(C,P) = 6.2 Hz; PCC*C*=), 128.8 (d, ^3J(C,P) = 10.0 Hz; *m*-Ph), 130.2 (d, ^4J(C,P) = 2.1 Hz; *p*-Ph), 132.6 (d, ^1J(C,P) = 30.8 Hz; *ipso*-Ph), 132.8 (d, ^2J(C,P) = 11.6 Hz; *o*-Ph), 195.8 (d, ^2J(C,P) = 8.3 Hz, ^1J(C,W) = 125.7 Hz; *cis*-CO), 198.4 (d, ^2J(C,P) = 29.9 Hz; *trans*-CO); ^{31}P NMR (101.25 MHz, $CDCl_3$): δ = −169.5 (^1J(P,W) = 253.0 Hz); IR (KBr): ν = 1923 (s/br, CO_{eq}), 1985 (w, CO_{eq}), 2072 (w, CO_{ax}); MS (70 eV): *m/z* (%): 538 (3) $[M]^+$, 482 (6) $[M - 2CO]^+$, 454 (8) $[M - 3CO]^+$, 426 (23) $[M - 4CO]^+$, 398 (85) $[M - 5CO]^+$; HR-MS (EI): calcd for $C_{19}H_{15}O_5P^{184}W$: 538.01672, found: 538.01634.

{1-(1'-Phenyl-1'-pentacarbonyltungstenphosphiran-2-yl)-7-phenyl-7-phosphadispiro-[2.0.2.1]hept-7-yl}pentacarbonyltungsten (28): 27d (55 mg, 0.10 mmol), complex **8** (133 mg, 0.20 mmol) and CuCl (10mg, 0.1 mmol) were heated in toluene (1 mL) at 55 °C for 6.5 h. Evaporation to dryness and chromatography of the residue over silica gel eluting with pentane/dichloromethane (4/1) yielded **28a** and **b** in a 5:3 ratio (60 mg, 62%) as a pale yellow oil; 12% of **27d** (7 mg) could be recovered. Subsequent chromatography on silica gel eluting with pentane/dichloromethane (9/1) and crystallization from hexane/DCM at 0 °C afforded colorless crystals of both isomers of **28**. ***Anti,anti*-(*R*,*R*-phosphiranyl-1*R*,3*S*,7*S*) and (*S*,*S*-phosphiranyl-1*S*,3*R*,7*R*)-isomer 28a**: m.p. 150 °C (decomp.); ^1H NMR (400.13 MHz, $CDCl_3$): δ = 0.85–0.98 (m, 2H; P*C*H, PCC*H*), 0.99–1.04 (m, 2H; CH_2), 1.44–1.62 (m, 1H; P*C*H_2; m, 4H; CH_2), 1.67 (ddd, ^2J(H,H) = 8.7 Hz, 1H; P*C*H_2), 7.38–7.45 (m, 8H; Ph*H*), 7.47–7.53 (m, 2H; *o*-Ph*H*); $^{13}C\{^1H\}$ NMR (100.62 MHz, $CDCl_3$): δ = 8.2 (d, ^2J(C,P) = 3.3 Hz; *C*H_2), 9.7 (s; *C*H_2), 16.0 (d, ^1J(C,P) = 11.6 Hz; P*C*H_2), 16.4 (s; *C*H_2), 24.2 (d, $^{(2+2)}J$(C,P) = 3.5 Hz; PC*C*H), 25.1 (s; P*C*), 27.4 (d, ^1J(C,P) = 16.2 Hz; P*C*H), 31.8 (dd, ^1J(C,P) = 3.8 Hz, ^3J(C,P) = 9.6 Hz; P*C*), 128.6

(d, ^3J(C,P) = 10.5 Hz; *m*-Ph), 129.1 (d, ^3J(C,P) = 10.0 Hz; *m*-Ph), 130.5 (d, ^4J(C,P) = 2.6 Hz; *p*-Ph), 130.8 (d, ^4J(C,P) = 2.1 Hz; *p*-Ph), 130.9 (d, ^1J(C,P) = 29.8 Hz; *ipso*-PhPCH$_2$), 132.2 (d, ^2J(C,P) = 13.4 Hz; *o*-Ph), 132.4 (d, ^2J(C,P) = 12.0 Hz; *o*-Ph), 133.7 (d, ^1J(C,P) = 22.3 Hz; *ipso*-Ph), 195.3 (d, ^2J(C,P) = 8.3 Hz, ^1J(C,W) = 125.6 Hz; *cis*-CO), 195.6 (d, ^2J(C,P) = 8.2 Hz, ^1J(C,W) = 125.7 Hz; *cis*-CO), 197.2 (d, ^2J(C,P) = 29.9 Hz; *trans*-CO), 197.8 (d, ^2J(C,P) = 30.8 Hz; *trans*-CO); ^{31}P NMR (101.25 MHz, $CDCl_3$): δ = –127.1 (^1J(P,W) = 258.7 Hz; *P*[3]triangulane), –164.0 (^1J(P,W) = 252.6 Hz; *P*CC); IR (KBr): ν = 1919, 1936 (s/br, CO_{eq}), 1983, 1993 (s/br, CO_{eq}), 2074 (m, CO_{ax}); elemental analysis for $C_{30}H_{20}O_{10}P_2{}^{184}W_2$: calcd (%): C 37.14, H 2.08; found: C 36.55, H 2.27. ***Anti,syn*-(*R*,*R*-Phosphiranyl-1*R*,3*S*,7*R*) and (*S*,*S*-phosphiranyl-1*S*,3*R*,7*S*)-isomer 28b**: m.p. 170 °C; ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 0.82–0.89 (m, 1H; PC*H*), 1.08–1.12 (m, 1H; PCC*H*), 1.19 (m, ^3J(H,P) = 5.2 Hz, 1H; CH_2), 1.21–1.38 (m, 3H; CH_2), 1.41–1.54 (m, 2H; CH_2), 1.67 (m, ^2J(H,P) = 1.0 Hz, 1H; PCH_2), 1.97 (m, ^2J(H,P) = 8.4 Hz, 1H; PCH_2), 7.37–7.41 (m, 6H; *m*-Ph*H*, *p*-Ph*H*), 7.48–7.54 (m, 4H; *o*-Ph*H*); ^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$): δ = 8.4 (d, ^2J(C,P) = 3.6 Hz; *C*H$_2$), 9.9 (s; *C*H$_2$), 15.2 (d, ^2J(C,P) = 4.6 Hz; *C*H$_2$), 15.8 (d, ^1J(C,P) = 11.4 Hz; P*C*H$_2$), 25.4 (d, ^2J(C,P) = 3.6 Hz; PC*C*H), 25.9 (s; P*C*), 27.3 (dd, ^1J(C,P) = 15.9 Hz, ^3J(C,P) = 2.3 Hz; P*C*H), 31.4 (dd, ^1J(C,P) = 5.3 Hz, ^3J(C,P) = 10.0 Hz; P*C*), 128.6 (d, ^3J(C,P) = 10.7 Hz; *m*-Ph), 128.9 (d, ^3J(C,P) = 10.1 Hz; *m*-Ph), 130.5 (d, ^4J(C,P) = 2.7 Hz; *p*-Ph), 130.7 (d, ^4J(C,P) = 2.1 Hz; *p*-Ph), 130.8 (d, ^1J(C,P) = 30.0 Hz; *ipso*-PhPCH$_2$), 132.5 (d, ^2J(C,P) = 13.7 Hz; *o*-Ph), 132.5 (d, ^2J(C,P) = 11.8 Hz; *o*-Ph), 132.6 (d, ^1J(C,P) = 21.1 Hz; *ipso*-Ph), 195.4 (d, ^2J(C,P) = 8.3 Hz, ^1J(C,W) = 125.5 Hz; *cis*-CO), 195.7 (d, ^2J(C,P) = 8.2 Hz, ^1J(C,W) = 125.7 Hz; *cis*-CO), 197.1 (d, ^2J(C,P) = 29.9 Hz; *trans*-CO), 197.9 (d, ^2J(C,P) = 30.6 Hz; *trans*-CO); ^{31}P NMR (101.25 MHz, $CDCl_3$): δ = –129.6 (^1J(P,W) = 259.7 Hz, ^4J(P,P) = 4.1 Hz; *P*[3]triangulane), –166.4 (^1J(P,W) = 251.6 Hz, ^4J(P,P) = 4.1 Hz; *P*CC); IR (KBr): ν = 1898, 1917 and 1927 (s/br, CO_{eq}), 2072 (m, CO_{ax}); MS (70 eV): *m/z* (%): 970 (20) [*M*]$^+$, 914 (5) [*M* – 2CO]$^+$, 858 (12) [*M* – 4CO]$^+$, 802 (24) [*M* – 6CO]$^+$, 746 (42) [*M* – 8CO]$^+$, 690 (55) [*M* – 10CO]$^+$; HR-MS (EI): calcd for $C_{30}H_{20}O_{10}P_2{}^{184}W_2$: 969.95520, found: 969.95191.

Crystal structure determinations. X-ray intensities were measured on a Nonius KappaCCD diffractometer with rotating anode and graphite monochromator (λ = 0.71073 Å). The structures were solved with automated Patterson Methods[34] (compounds **7**, **12a**, **14**, **16b**, **21a**, and **28a**) or Direct Methods[35] (compound **17a**) and refined with SHELXL-97[36] on F^2 of all reflections. Geometry calculations, drawings and checking for higher symmetry were performed with the PLATON[37] package.

Compound 7. $C_{25}H_{21}O_5PW$, Fw = 616.24, colourless needle, 0.51 x 0.24 x 0.21 mm^3, monoclinic, $P2_1/c$ (no. 14), a = 8.0553(1), b = 17.0487(2), c = 18.6096(3) Å, β = 114.6694(12)°, V = 2322.45(6) Å^3, Z = 4, ρ = 1.762 g/cm^3. Temperature 110(2) K. 54513 reflections were measured up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.81 Å^{-1}. An analytical absorption correction was applied (μ = 5.08 mm^{-1}, 0.15-0.40 correction range). 10119 reflections were unique (R_{int} = 0.049). Non-hydrogen atoms were refined freely with anisotropic displacement

parameters. All hydrogen atoms were located in the difference Fourier map. Phenyl hydrogen atoms were refined as rigid groups, all other hydrogen atoms were refined freely with isotropic displacement parameters. 353 parameters were refined with no restraints. R1/wR2 [$I > 2\sigma(I)$]: 0.0188/0.0416. R1/wR2 [all refl.]: 0.0412/0.0533. S = 0.603. Residual electron density between -1.32 and 1.63 e/Å^3.

Compound 12a. $C_{17}H_{13}O_5PW$, Fw = 512.09, colourless plate, 0.18 x 0.13 x 0.06 mm^3, monoclinic, $P2_1/c$ (no. 14), a = 9.8460(1), b = 9.2242(1), c = 38.9935(3) Å, β = 97.1897(3)°, V = 3513.60(6) Å^3, Z = 8, ρ = 1.936 g/cm^3. Temperature 150(2) K. 44020 reflections were measured up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 Å^{-1}. An analytical absorption correction was applied (μ = 6.69 mm^{-1}, 0.32-0.79 correction range). 7989 reflections were unique (R_{int} = 0.041). Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in the difference Fourier map. Phenyl hydrogen atoms were refined as rigid groups, all other hydrogen atoms were refined freely with isotropic displacement parameters. 497 parameters were refined with no restraints. R1/wR2 [$I > 2\sigma(I)$]: 0.0211/0.0432. R1/wR2 [all refl.]: 0.0310/0.0461. S = 1.026. Residual electron density between -1.19 and 1.03 e/Å^3.

Compound 14. $C_{19}H_{15}O_5PW$, Fw = 538.13, colourless block, 0.33 x 0.15 x 0.15 mm^3, monoclinic, C2/c (no. 15), a = 24.8645(2), b = 10.0503(1), c = 18.0840 Å, β = 122.9428(4)°, V = 3792.50(7) Å^3, Z = 8, ρ = 1.865 g/cm^3. Temperature 150(2) K. 32020 reflections were measured up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 Å^{-1}. An analytical absorption correction was applied (μ = 6.20 mm^{-1}, 0.21-0.43 correction range). 4335 reflections were unique (R_{int} = 0.039). Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in the difference Fourier map. Phenyl hydrogen atoms were refined as rigid groups, all other hydrogen atoms were refined freely with isotropic displacement parameters. 275 parameters were refined with no restraints. R1/wR2 [$I > 2\sigma(I)$]: 0.0165/0.0365. R1/wR2 [all refl.]: 0.0192/0.0374. S = 1.097. Residual electron density between -1.03 and 0.68 e/Å^3.

Compound 16b. $C_{18}H_{13}O_5PW$, Fw = 524.10, colourless needle, 0.36 x 0.09 x 0.06 mm^3, triclinic, $P\overline{1}$ (no. 2), a = 9.9006(10), b = 14.0474(12), c = 14.652(2) Å, α = 64.984(8), β = 79.165(9), γ = 89.522(8)°, V = 1807.9(3) Å^3, Z = 4, ρ = 1.926 g/cm^3. Temperature 150(2) K. 41602 reflections were measured up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.59 Å^{-1}. An analytical absorption correction was applied (μ = 6.50 mm^{-1}, 0.24-0.86 correction range). The crystal appeared to be non-merohedrally twinned with a twofold rotation about the a-axis as twin operation. This twin relationship was taken into account for the integration[38] and merging[39] of the reflections and the HKLF5 refinement[40]. 11455 reflections were unique (R_{int} = 0.071). Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in the difference Fourier map and refined as rigid groups. 452 parameters were refined with no restraints. R1/wR2 [$I > 2\sigma(I)$]: 0.0422/0.1208. R1/wR2 [all refl.]:

0.0746/0.1343. S = 1.084. Twin fraction 0.1862(5). Residual electron density between -1.36 and 2.04 e/Å^3.

Compound 17a. $C_{29}H_{18}O_{10}P_2W_2$, Fw = 956.07, colourless needle, 0.42 x 0.12 x 0.12 mm^3, monoclinic, $P2_1$ (no. 4), a = 6.3432(4), b = 21.233(2), c = 11.6997(8) Å, β = 98.997(7)°, V = 1556.4(2) Å^3, Z = 2, ρ = 2.040 g/cm^3. Temperature 150(2) K. 18806 reflections were measured up to a resolution of (sin $\theta/\lambda)_{max}$ = 0.65 Å^{-1}. An absorption correction based on multiple measured reflections was applied (μ = 7.54 mm^{-1}, 0.18-0.41 correction range). 7049 reflections were unique (R_{int} = 0.026). Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were introduced in calculated positions and refined as rigid groups. 388 parameters were refined with 1 restraint. R1/wR2 [I > 2σ(I)]: 0.0296/0.0667. R1/wR2 [all refl.]: 0.0359/0.0699. S = 1.018. Flack x parameter[41] -0.024(8). Residual electron density between -1.79 and 1.26 e/Å^3.

Compound 21a. $C_{19}H_{15}O_5PW$, Fw = 538.13, colourless needle, 0.20 x 0.08 x 0.04 mm^3, triclinic, $P\overline{1}$ (no. 2), a = 9.1520(1), b = 9.2457(1), c = 11.7216(2) Å, α = 79.5224(9), β = 72.9620(8), γ = 84.7207(7)°, V = 931.71(2) Å^3, Z = 2, ρ = 1.918 g/cm^3. Temperature 150(2) K. 16007 reflections were measured up to a resolution of (sin $\theta/\lambda)_{max}$ = 0.65 Å^{-1}. An analytical absorption correction was applied (μ = 6.31 mm^{-1}, 0.39-0.77 correction range). 4172 reflections were unique (R_{int} = 0.045). Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in the difference Fourier map. Phenyl hydrogen atoms were refined as rigid groups, all other hydrogen atoms were refined freely with isotropic displacement parameters. 275 parameters were refined with no restraints. R1/wR2 [I > 2σ(I)]: 0.0192/0.0386. R1/wR2 [all refl.]: 0.0236/0.0397. S = 1.054. Residual electron density between -0.84 and 0.98 e/Å^3.

Compound 28a. $C_{30}H_{20}O_{10}P_2W_2$ + disordered solvent, Fw = 970.10[*], yellowish needle, 0.42 x 0.18 x 0.18 mm^3, monoclinic, C2/c (no. 15), a = 30.9063(16), b = 11.9175(8), c = 20.6181(11) Å, β = 117.985(7)°, V = 6706.2(8) Å^3, Z = 8, ρ = 1.922 g/cm^3[*]. Temperature 150(2) K. 49557 reflections were measured up to a resolution of (sin $\theta/\lambda)_{max}$ = 0.65 Å^{-1}. An absorption correction based on multiple measured reflections was applied (μ = 7.00 mm^{-1}[*], 0.17-0.28 correction range). Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in the difference Fourier map. Phenyl hydrogen atoms were refined as rigid groups, all other hydrogen atoms were refined freely with isotropic displacement parameters. The crystal structure contains large voids (545 Å^3/unit cell) filled with disordered CH_2Cl_2 solvent molecules. Their contribution to the structure factors was secured by back-Fourier transformation using the SQUEEZE routine of the PLATON program[37] resulting in 152 electrons / unit cell. 437 parameters were refined with no restraints. R1/wR2 [I > 2σ(I)]: 0.0190/0.0370. R1/wR2 [all refl.]: 0.0297/0.0386. S = 1.030. Residual electron density between -0.64 and 0.76 e/Å^3.

[*] Derived quantities do not contain the contribution of the disordered solvent.

CCDC 212086 (compound **7**), 269693 (**12a**), 269694 (**14**), 269695 (**16b**), 269696 (**17a**), 269697 (**21a**) and 269698 (**28a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

4.7 References and Notes

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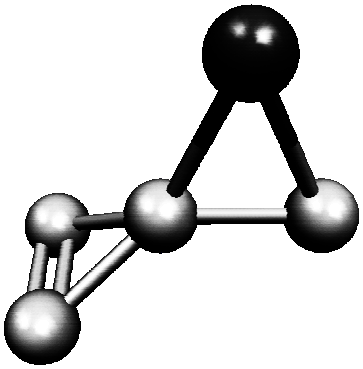
Phosphaspiropentene as a Transient Intermediate

5

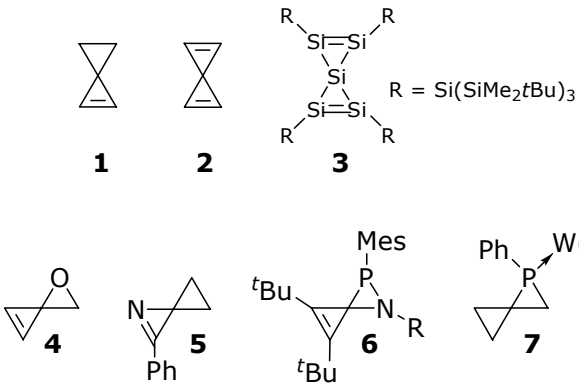
Cyclopropene substituents destabilize the PCC ring, much in contrast to cyclopropane substituents, which have a stabilizing effect (chapter 3 and 4). This becomes evident by the addition of dichlorocarbene to a phosphatriafulvene where a phospha-spiropentene (see picture) is the plausible kinetic product, but rearranges to a novel P-substituted triafulvene. The calculated barrier of 18.6 kcal·mol^{-1} for this process is consistent with the temperature of –40 °C at which this reaction proceeds.



Published in: *Organometallics,* **2005**, *24*, 5172–5175.

5.1 Introduction

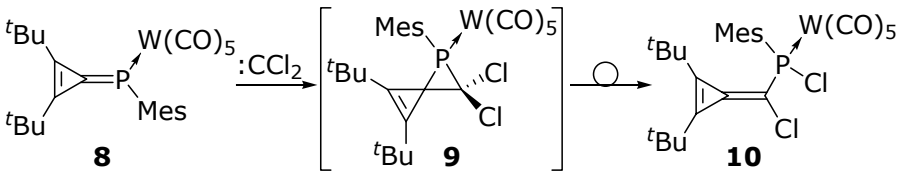
Spiro-connected cycloalkenes exhibit intriguing bonding and electronic properties due to spiroconjugation.[1] Although the smallest of these highly strained hydrocarbons, spiropentene (**1**)[2] and spiropentadiene (**2**),[3] have been reported, spirenes with heteroatoms are extremely rare. Only recently, the thermally stable spiropentasiladiene **3** was reported.[4] Examples with other heteroatoms are limited to 1-oxaspiropent-4-enes, including the parent **4**,[5] and 1-azaspiropent-1-ene **5**,[6] but none with a phosphorus atom are known other than the 1-aza-2-phospha-spiro[2.2]pentene **6**, which was postulated as a transient in the formation of 1*H*-2-iminophosphetes.[7] In contrast, P-containing spiranes carrying a transition-metal complex, e.g. the phosphaspiropentane **7**,[8] are stable, which is highlighted for the extended arrays[9] by a phospha[7]triangulane that consists of seven spiro-connected three-membered rings and has a melting point above 150 °C.[10]



5.2 Results and Discussion

Can a transition-metal complex likewise stabilize a P-containing spirene? To explore this, we examine the chemistry of 1-phosphaspiropent-4-ene. Access to this compound can be envisioned by addition of dichlorocarbene, generated in situ from *t*-BuOK/$CHCl_3$,[11] to the exocyclic P=C bond[12] of phosphatriafulvene complex **8**[13] (0 °C, pentane). This reaction yielded, instead, the novel P-substituted triafulvene **10** (95%, colorless crystals) and showed no trace of phosphaspiropentene **9**, not even by ^{31}P NMR monitoring of the reaction at –40 °C (Scheme 1). Triafulvene **10** has distinctive resonances at $\delta^{31}P$ = 110.0 (^1J(P,W) = 282.7 Hz) and $\delta^{13}C$ = 86.6 (^1J(C,P)

= 52.5 Hz), 135.2 (d, ^2J(C,P) = 9 Hz), 146.0 (s), and 147.4 (^3J(C,P) = 6.4 Hz).[14] P–C bond rotation of the mesityl-group is hindered, causing a broad signal at δ^1H (293K) = 2.54 for the *ortho*-methyl groups that narrows at higher temperatures. The single-crystal X-ray structure (Figure 1) shows a shortened P1–C1 bond (1.782(3) Å) and the cyclopropene ring being nearly coplanar with the Cl2–C1–P1 plane with a C3–C2–C1–P1 torsion angle of –1.4(8)°. Normal C=C bonds (C1–C2 1.331(4), C3–C4 1.331(4) Å), indicate a diminished π-delocalization, which is confirmed by the calculated NICS value of only –21.4, which is considerably less negative than that of cyclopropene (–28.4).



Scheme 1. Synthesis of triafulvene **10**.

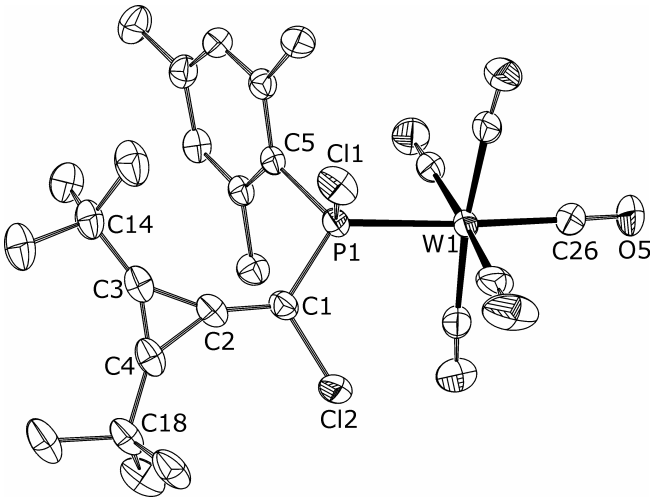
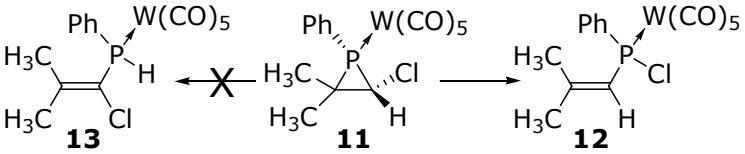


Figure 1. Displacement ellipsoid plot of **10** with ellipsoids drawn at the 50% probability level. Hydrogen atoms and the pentane solvent molecule are omitted for clarity. Selected bond lengths [Å], angles and torsion [°]: W1–P1 2.4987(7), Cl1–P1 2.0920(10), Cl2–C1 1.774(3), P1–C1 1.782(3), P1–C5 1.837(3), C1–C2 1.331(4), C2–C3 1.433(4), C2–C4 1.425(4), C3–C4 1.331(4); Cl2–C1–P1 115.04(15), C2–C3–C4 62.0(2), C3-C2-C4 55.49(19), C2-C4-C3 62.5(2); C3-C2-C1-P1 –1.4(8).

Is phosphaspiropentene **9** an intermediate in the formation of **10**? Such a rearrangement does convert the phosphirane complex **11** into **12** (Scheme 2), but, at the much higher temperature of 110 °C.[15] We examine both processes using theoretical methods.



Scheme 2. Rearrangements of phosphirane **11**.

A large barrier of 71.3 kcal/mol (B3LYP/6–31G**) has been reported for converting the parent **11'** into **12'** (H for Me and Ph; without $W(CO)_5$) by P–C bond cleavage with a concurrent Cl-shift from C to P,[16] which, of course, does not comply with the experimental observations,[15] nor does the calculated favored H-shift that would give **13**. Clearly, the transition-metal group has a major influence, which we substantiate using BP86/6–31G**(LANL2DZ) calculations.[17]

Adding the singlet phosphinidene Ph-P=$W(CO)_5$ to 1-chloro-2-methylpropene gives **11**, likely by a barrier-free non-least-motion trajectory,[18] with less exothermicity (23.0 kcal·mol^{-1}) than for the parent ethylene (35.9 kcal·mol^{-1}),[19] due to the reduced nucleophilicity of 1-chloro-2-methylpropene. Converting structure **11** in a single step to the 20.9 kcal·mol^{-1} more stable vinylchlorophosphine **12**, in which the chloride anti to the P-$W(CO)_5$ group migrates to phosphorus, requires a 24.0 kcal·mol^{-1} barrier to be overcome (Figure 2). Converting phosphirane **11** into vinylphosphine **13**, by migrating H instead of Cl, has only a marginal exothermicity (3.2 kcal·mol^{-1}) and a higher barrier ($\Delta E^{\ddagger}$ = 39.1 kcal·mol^{-1}), suggesting this to be a less likely process, which concurs with the experimental observations. The barrier for rearranging **11** into **12** is comparable to the dissociation energy to regenerate Ph-P=$W(CO)_5$ and 1-chloro-2-methylpropene (23.0 kcal·mol^{-1}), which clarifies the modest isolated yields for **11** (11 %) and **12** (39 %).[15]

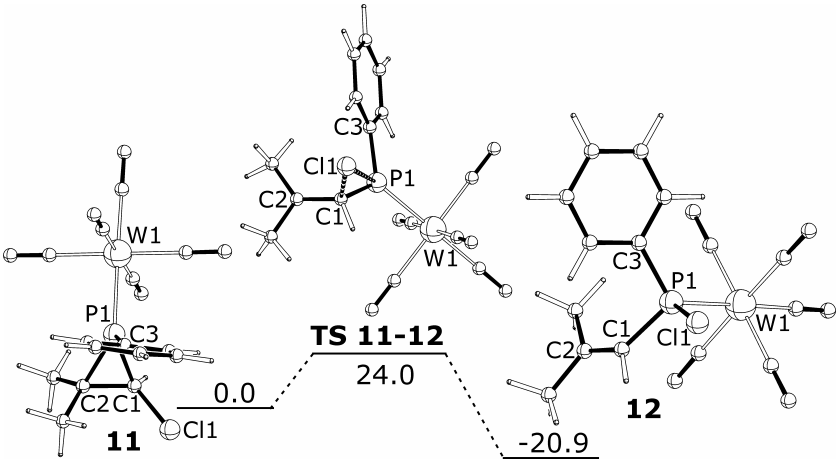
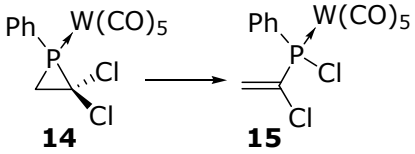


Figure 2. Relative BP86/6–31G** (LANL2DZ for W) energies (ZPE corrected, in kcal·mol^{-1}) for the conversion of **11** into **12**. Selected bond lengths [Å] of **11**: W1-P1 2.539, P1-C1 1.877, P1-C2 1.909, P1-C3 1.834, C1-Cl1 1.785, C1-C2 1.539; **TS***anti*Cl-shift (**TS11**→**12**): W1-P1 2.475, P1-Cl1 3.508, P1-C1 1.782, P1-C2 2.751, P1-C3 1.806, C1-Cl1 2.313, C1-C2 1.418; **12**: W1-P1 2.527, P1-Cl1 2.133, P1-C1 1.832, P1-C3 1.846, C1-C2 1.356.

In contrast, the analogous phosphirane **14** does not rearrange thermally and a $Pd(PPh_3)_4$-catalyzed reaction is needed (85 °C) to afford vinylchlorophosphine **15** (Scheme 3).[15] BP86/6–31G**(LANL2DZ) calculations reveal that converting structure **14** to the 18.6 kcal·mol^{-1} more stable vinylchlorophosphine **15**, in which the chloride anti to the P-$W(CO)_5$ group migrates to phosphorus,[20] is more demanding than the rearrangement of **11** and requires 31.5 kcal·mol^{-1}. This barrier is much higher than the dissociation energy needed to regenerate Ph-P=$W(CO)_5$ and 1,1-dichloroethene (23.2 kcal·mol^{-1}), explaining why this reaction does not proceed thermally.



Scheme 3. Rearrangement of phosphirane **14**.

Extending the calculations to the addition of CCl_2 to phosphatriafulvene **8''** (H for *t*Bu, Ph for mesityl; labeled **''**) indicates a large exothermicity (52.3 kcal·mol^{-1}) for the formation of phosphaspiropentene **9''**. We note that the addition of Ph-P=$W(CO)_5$ to 3,3-dichlorotriafulvene, which would also give **9''**, is less exothermic (22.9 kcal·mol^{-1}), because metal complexation reduces the reactivity of phosphinidenes.[21] Without the $W(CO)_5$-group, ^{1}PPh (A_1) adds to 3,3-dichlorotriafulvene with a reaction energy of −71.7 kcal·mol^{-1}.

The single-step conversion of the $W(CO)_5$-complexed phosphaspiropentene **9''** into chlorophosphine **10''** is more easily ($\Delta E^{\ddagger}$ = 18.6, ΔE = −24.7 kcal·mol^{-1}, Figure 3)[22] than the analogous **14**→**15** rearrangement ($\Delta E^{\ddagger}$ = 31.5 kcal·mol^{-1}), and is favored by 4.6 kcal·mol^{-1} over the dissociation into Ph-P=$W(CO)_5$ and 3,3-dichlorotriafulvene. The higher reactivity of **9''** compared to that of **11** and **14** can be rationalized by the destabilization of the phospirene ring upon spirofusion. Both the phosphorus[23] and the electron-withdrawing chloro substituents activate phosphirene **14** (NICS = −34.8) compared to the parent cyclopropene[24] (NICS = −42.8); additional spirofusion in **9''** further reduces the σ-aromaticity (NICS = −26.9). This effect is also reflected by the elongated distal and proximal P–C bonds[9] (P1–C1 1.927, P1–C2 1.866 Å) as compared to the corresponding bond lengths of **14** (P1–C1 1.897, P1–C2 1.847 Å) and phosphaspiropentane **7**[8] (experimental: P1–C1 1.855, P1–C2 1.794 Å).

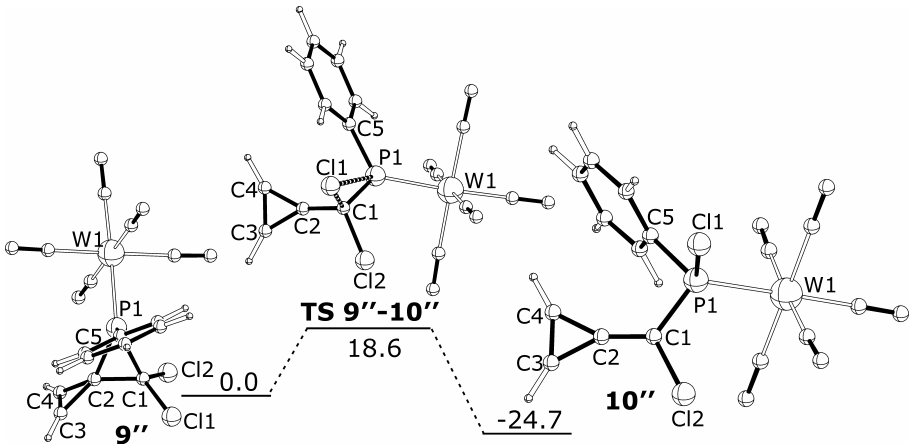


Figure 3. Relative BP86/6–31G** (LANL2DZ for W) energies (ZPE corrected, in kcal·mol^{-1}) for the conversion of **9''** into **10''**. Selected bond lengths [Å] of **9''**: W1-P1 2.520, P1-C1 1.927, P1-C2 1.866, P1-C5 1.834, C1-Cl1 1.789, C1-Cl2 1.791, C1-C2 1.498, C2-C3 1.489, C2-C4 1.491,

C3-C4 1.312; **TS9"-10"**: W1-P1 2.497, P1-Cl1 3.525, P1-C1 1.810, P1-C2 2.536, P1-C5 1.826, C1-Cl1 2.239, C1-Cl2 1.783, C1-C2 1.416, C2-C3 1.426, C2-C4 1.420, C3-C4 1.344; **10"**: W1-P1 2.517, P1-Cl1 2.141, P1-C1 1.814, P1-C5 1.854, C1-Cl2 1.771, C1-C2 1.350, C2-C3 1.442, C2-C4 1.438, C3-C4 1.335.

5.3 Conclusion

Phosphaspiropentene **9** is the plausible kinetic product that results from addition of dichlorocarbene to phosphatriafulvene **8**. The calculated barrier of 18.6 kcal·mol^{-1} for rearrangement to the more stable P-substituted triafulvene **10** is consistent with the temperature of –40 °C at which the reaction proceeds. Currently, we are testing other carbenes to obtain the, as yet, elusive phosphaspiropentenes.

5.4 Computational Section

All density functional theory calculations (BP86) were performed with the Gaussian98 suite of programs,[17] using the LANL2DZ basis and pseudopotentials for tungsten and the 6-31G** basis set for all other atoms. The natures of all transition structures were confirmed with frequency calculations. Intrinsic reaction coordinate (IRC) calculations were performed to ascertain the connection between reactant and product. The nucleus independent chemical shift[25] (NICS) values were calculated at the B3LYP/6-311G+(2p,d) level, leaving out the substituents.

5.5 Experimental Section

NMR spectra were recorded on a Bruker Advance 250 (^{31}P; 85% H_3PO_4) and a MSL 400 (^{1}H, ^{13}C) and referenced internally to residual solvent resonances (^{1}H, δ 7.25 ppm ($CDCl_3$); $^{13}C\{^1H\}$, 77.0 ppm ($CDCl_3$)). The IR spectrum was recorded on a Mattson-6030 Galaxy FT-IR spectrophotometer, and the high-resolution mass spectrum (HR-MS) was performed on a Finnigan Mat 900 mass spectrometer operating at an ionization potential of 70 eV. The melting point of **10** was measured on a sample in an unsealed capillary and is uncorrected.

10: $CHCl_3$ (56 µL, 0.7 mmol) was added under nitrogen at 0 °C to a solution of **8**[7] (87 mg, 0.14 mmol) and *t*-BuOK (79 mg, 0.7 mmol) in dry pentane (3 mL). After additional stirring for 30 min at 0 °C and another 30 min at room temperature, the reaction mixture was filtered and concentrated and **10** could be obtained as colorless crystals in 95 % yield (104 mg; = **10**·pentane) after crystallization at – 20 °C. **10**: m.p. 100 °C (decomp); $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, 293 K): δ = 110.0 (^1J(P,W) = 282.7 Hz); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 328 K): δ = 20.5 (s; *p*-CH_3-ArP), 24.5 (d, ^3J(C,P) = 5.4 Hz; *o*-CH_3-ArP), 28.4 (s; C(CH_3)$_3$), 29.6 (s; C(CH_3)$_3$), 32.3 (s; $C(CH_3)_3$), 32.4 (d, ^4J(C,P) = 0.8 Hz; $C(CH_3)_3$), 86.6 (d, ^1J(C,P) = 52.5 Hz;

=*C*Cl), 131.4 (d, ^3J(C,P) = 7.3 Hz; *m*-ArP), 135.2 (d, ^2J(C,P) = 9 Hz; *o*-ArP), 135.2 (d, ^2J(C,P) = 9 Hz; *C*=CCl), 135.7 (d, ^1J(C,P) = 26.8 Hz; *ipso*-ArP), 139.9 (d, ^4J(C,P) = 1.5 Hz; *p*-ArP), 146.0 (s; =*C*-C(CH$_3$)$_3$), 147.4 (d, ^3J(C,P) = 6.4 Hz; =*C*-C(CH$_3$)$_3$), 196.8 (d, ^2J(C,P) = 7.3 Hz, ^1J(C,W) = 127.2 Hz; *cis*-CO), 200.3 (d, ^2J(C,P) = 31.1 Hz, ^1J(C,W) = 141.6 Hz; *trans*-CO); ^{1}H NMR (400.1 MHz, $CDCl_3$, 328 K): δ = 0.86 (s, 9H; C(C*H*$_3$)$_3$), 1.40 (s, 9H; C(C*H*$_3$)$_3$), 2.25 (s, 3H; *p*-C*H*$_3$-ArP), 2.54 (br. s, 6H; *o*-C*H*$_3$-ArP), 6.84 (d, ^4J(H,P) = 4.2 Hz, 2H; *m*-ArP); IR (KBr): ν = 1939 (s/br, CO_{eq}), 2074 cm^{-1} (w, CO_{ax}); HR-MS (EI, 70 eV): *m/z* (%): 706 (0.5) $[M]^+$, 671 (0.5) $[M - Cl]^+$, 566 (10) $[M - 5CO]^+$; calcd for $[M^+ - 5CO]$: 566.0893, found: 566.0900.

Crystal structure determination of compound **10**, $C_{26}H_{29}Cl_2O_5PW \cdot 0.5C_5H_{12}$, Fw = 743.28, colorless needle, 0.42 × 0.24 × 0.06 mm^3. Monoclinic crystal system, space group C2/c (no. 15). Cell parameters: a = 19.0406(2), b = 18.9032(2), c = 19.5695(2) Å, β = 117.0955(5)°, V = 6270.57(11) $Å^3$. Z = 8, ρ = 1.575 g/cm^3. 71511 reflections were measured up to $(\sin\theta/\lambda)_{max}$ = 0.65 $Å^{-1}$ on a Nonius KappaCCD with rotating anode (graphite monochromator, Mo-K_α, λ = 0.71073 Å) at a temperature of 150 K. An analytical absorption correction was applied (μ = 3.94 mm^{-1}, 0.27-0.72 correction range). 7212 reflections were unique (R_{int} = 0.049). The structure was solved with automated Patterson methods with the program DIRDIF99[26] and refined with the program SHELXL97[27] against F^2 of all reflections. Non hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in the difference Fourier map and were refined as rigid groups. The pentane solvent molecule is located on a twofold axis in the unit cell. 348 refined parameters, 20 restraints. R [$I > 2\sigma(I)$]: R1 = 0.0237, wR2 = 0.0545. R [all refl.]: R1 = 0.0321, wR2 = 0.0586. GoF = 1.065. Residual electron density between –1.52 and 0.94 e/$Å^3$. The drawings, geometry calculations, and checking for higher symmetry was performed with the program PLATON.[28]

5.6 References and Notes

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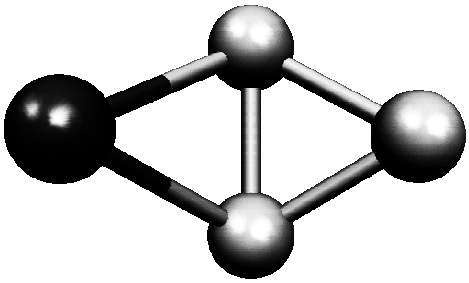
Valence Isomerization of 2-Phospha[1.1.0]bicyclobutanes

6

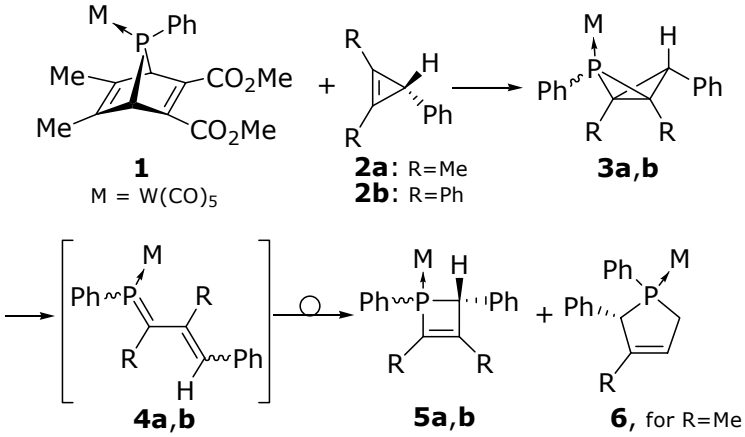
2-Phosphabicyclo[1.1.0]butanes (see picture), synthesized from the complexed phosphinidene Ph-P=$W(CO)_5$ and cyclopropenes, are remarkably stable compounds that valence isomerize to 3-phosphacyclobutenes via 1-phosphabutadienes at elevated temperatures. Different from the hydrocarbon analogues for which the *trans*-butadiene is the favored product, the 1-phosphabutadiene intermediate is trappable as a phospholene due to rearrangements, which are specific for the phosphorus compounds.



Published in: *Angew. Chem.* **2005**, *117*, 6737–6740; *Angew. Chem. Int. Ed.* **2005**, *44*, 6579–6582.

6.1 Introduction

The unique electronic properties of the strained bicyclo[1.1.0]butanes[1] are enhanced by the heteroatoms in the molecular frame. Illustrative is the bond-stretch isomerization of the P_2C_2 and P_2B_2 bicycles.[2] However, very few systems are known with a single heteroatom,[3] probably because of their high reactivity, which is only moderated when the heteroatom occupies a bridgehead position as in the 1-aza derivatives.[4] The increased reactivity of the hetero systems is due to the valence isomerization to which the bicyclo[1.1.0]butanes are prone. We now report on the first 2-phospha derivatives.



Scheme 1. Synthesis of 2-phosphabicyclo[1.1.0]butanes **3**.

6.2 Synthesis of 2-phosphabicyclo[1.1.0]butanes

The carbene-like phosphinidene Ph-P=$W(CO)_5$[5] was generated in situ by cheletropic elimination from **1** at 110 °C in toluene and then allowed to react with cyclopropene **2a**[6] (Scheme 1). This led to the desired $W(CO)_5$-complexed 2-phospha-bicyclo[1.1.0]butanes *exo*-**3a** (δ^{31}P = – 85.1 ppm) and *endo*-**3a** (δ^{31}P = – 36.7 ppm)[7] in a 10:9 ratio, which were isolated in 69 % yield as colorless solids. The remarkably stable products were characterized by single-crystal X-ray analyses, which showed puckered geometries with P1–C1–C2–C3 folding angles of –114.66(15)° for *exo*-**3a** and –120.65(14)° for *endo*-**3a**, and transannular C1–C2 bonds of 1.516(3) and 1.550(3) Å, respectively (Figure 1). The flatter *endo* structure

with the longer C1–C2 bond is the least stable of the two and decomposes at about 130 °C. At this temperature, the *exo* isomer undergoes valence isomerization to give 3-phosphacyclobutene complexes *cis*-**5a** (δ^{31}P = 46.3 ppm) and *trans*-**5a** (δ^{31}P = 55.2 ppm, ^{2}J(H,P) = 9.5 Hz)[8] in a 4:1 ratio (35 %) besides phospholene complex **6** (41 %, δ^{31}P = 37.9 ppm) as major product. Formation of the phospholene was confirmed by a crystal structure analysis (Figure 2).

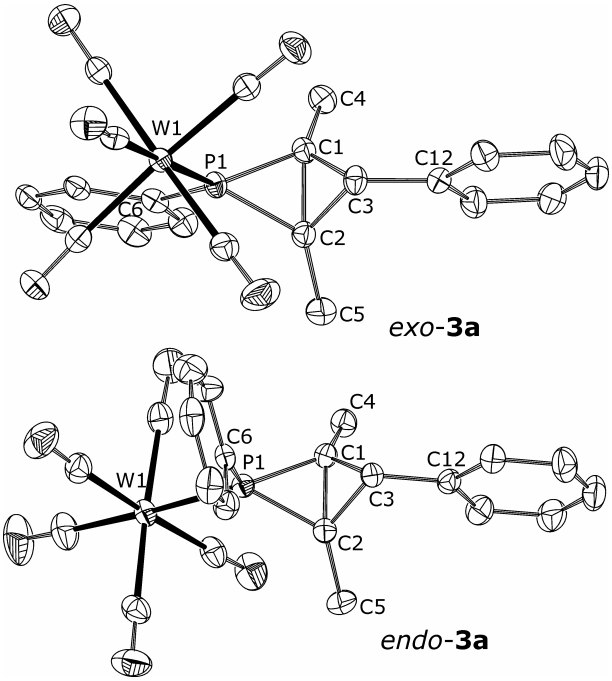


Figure 1. Displacement ellipsoid plot of *exo*- and *endo*-**3a** with ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å], angles and torsion angles [°] for *exo*-**3a**: W1-P1 2.5013(6), P1-C1 1.808(2), P1-C2 1.811(2), P1-C6 1.820(2), C1-C2 1.516(3), C1-C3 1.515(3), C1-C4 1.500(3), C2-C3 1.512(3), C2-C5 1.505(3), C3-C12 1.488(3); C1-P1-C2 49.52(10), P1-C1-C2 65.35(12), P1-C1-C3 96.79(15), C2-C1-C3 59.83(15), C2-C1-C4 139.6(2), P1-C2-C1 65.13(12), P1-C2-C3 96.78(15), C1-C2-C3 60.06(15), C1-C2-C5 141.4(2), C1-C3-C2 60.11(15); P1-C1-C2-C3 –114.66(15). *Endo*-**3a**: W1-P1 2.4851(5), P1-C1 1.801(2), P1-C2 1.792(2), P1-C6 1.823(2), C1-C2 1.550(3), C1-C3 1.511(3), C1-C4 1.502(3), C2-C3 1.521(3), C2-C5 1.500(3), C3-C12 1.495(3); C1-P1-C2 51.11(9), P1-C1-C2 64.13(11), P1-C1-C3 100.05(14), C2-C1-C3 59.57(14), C2-C1-C4 135.80(19), P1-C2-C1 64.76(11), P1-C2-C3 100.08(13), C1-C2-C3 58.94(13), C1-C2-C5 136.7(2), C1-C3-C2 61.49(13); P1-C1-C2-C3 –120.65(14).

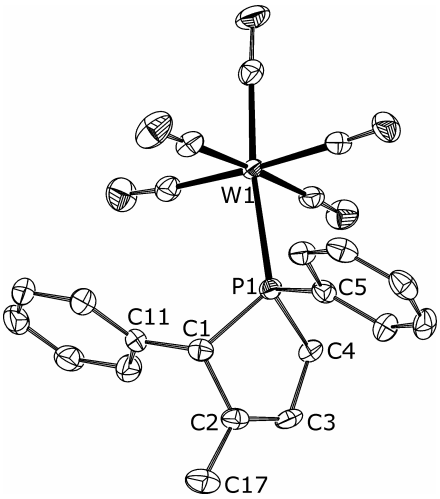


Figure 2. Structure of **6** in the crystal, one of the two crystallographically independent molecules is shown (displacement ellipsoids drawn at the 50% probability level; hydrogen atoms omitted for clarity). Selected bond lengths [Å], angles and torsion angles [°] with the second independent molecule in square brackets: W1-P1 2.5158(8) [2.5073(8)], P1-C1 1.871(3) [1.870(3)], P1-C4 1.830(3) [1.832(3)], P1-C5 1.828(3) [1.829(3)], C1-C2 1.517(4) [1.527(4)], C1-C11 1.509(4) [1.517(4)], C2-C3 1.323(4) [1.311(4)], C2-C17 1.507(4) [1.507(4)], C3-C4 1.505(4) [1.503(4)]; C1-P1-C4 92.21(13) [92.09(13)], P1-C1-C2 102.25(19) [102.71(19)], C1-C2-C3 116.0(3) [115.6(3)], C2-C3-C4 116.8(3) [117.5(3)], P1-C4-C3 103.7(2) [103.7(2)]; P1-C1-C2-C3 –21.0(3) [-19.1(3)], C1-C2-C3-C4 1.9(4) [0.0(4)], C11-C1-C2-C3 100.9(3) [104.0(3)].

6.3 Mechanism

BP86/6–31G*(LANL2DZ) calculations[9] on model structures (labeled **'**, without C-substituents) did not demonstrate a direct path from **3** to **5**,[10] but instead the involvement of 1-phosphabutadiene **4** was established. Isomerization of *exo*-**3'** to give *trans*-**4'** proceeds by a concerted, asynchronous conrotatory ring opening (ΔE = –18.4, $\Delta E^{\ddagger}$ = 32.8 kcal·mol^{-1}; Figure 3). With subsequent conrotatory electrocyclic ring closure, via the *gauche*-form of **4'** (ΔE = 3.7, $\Delta E^{\ddagger}$ = 7.9 kcal·mol^{-1}), the more stable phosphacyclobutene **5'** is formed (ΔE = –4.4, $\Delta E^{\ddagger}$ = 19.2 kcal·mol^{-1}). This route implies that 1-phosphabutadiene **4** is a reaction intermediate. The concerted, asynchronous conrotatory ring opening with an initial CH_2 group rotation was found to be higher in energy (ΔE = –17.4, $\Delta E^{\ddagger}$ = 39.7 kcal·mol^{-1}).

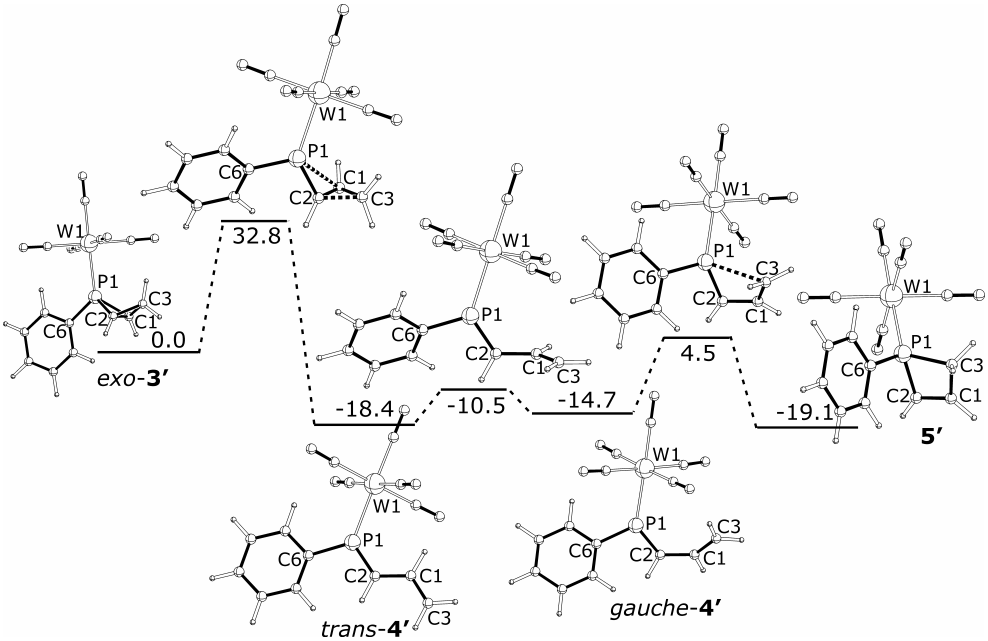
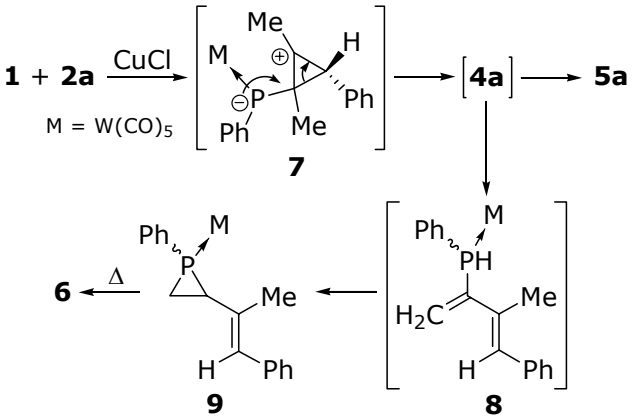


Figure 3. Relative BP86/6–31G* (LANL2DZ for W) energies (ZPE corrected, in kcal·mol^{-1}) for the rearrangement of *exo*-**3'** into **5'**. Selected bond lengths [Å], angles and torsion angles [°] of *exo*-**3'** (C_s): W1-P1 2.536, P1-C1 1.833, P1-C6 1.846, C1-C2 1.527, C1-C3 1.506, C1-P1-C2 49.2, C1-C3-C2 60.9, P1-C1-C2-C3 120.2; **TS***exo*-**3'**–*trans*-**4'**: W1-P1 2.541, P1-C1 2.709, P1-C2 1.801, P1-C6 1.820, C1-C2 1.474, C1-C3 1.446, C2-C3 1.595; *trans*-**4'** (C_s): W1-P1 2.515, P1-C2 1.703, P1-C6 1.830, C1-C2 1.441, C1-C3 1.359; **TS***trans*-**4'**–*gauche*-**4'**: P1-C2-C1-C3 95.2; *gauche*-**4'**: P1-C2-C1-C3 31.0; **TS***gauche*-**4'**–**5'**: W1-P1 2.568, P1-C2 1.774, P1-C3 2.558, C1-C2 1.391, C1-C3 1.419, P1-C2-C1-C3 26.4; **5'**: W1-P1 2.539, P1-C2 1.838, P1-C3 1.915, P1-C6 1.848, C1-C2 1.355, C1-C3 1.518.

The small energy difference between **4'** and 3-phosphacyclobutene **5'** is reflected in Mathey's[11] use of derivatives of **5** as masked 1-phosphabutadienes.[12] These results highlight that the stability order **3'** << **4'** < **5'** of the three valence isomers differs from the established values for the hydrocarbons (**3''** << **5''** << **4''**).[13]

6.4 CuCl Catalysis

To gain more insight into the formation of phospholene **6**, we resorted to the more gentle CuCl-catalyzed reaction of **1**[5,14] with **2a** (55 °C, 15 h; Scheme 2). This reaction gave, with the exception of **6**, the same products as the noncatalyzed reaction, that is, *exo*- and *endo*-**3a** (4:1 ratio, 16 %) and *cis*- and *trans*-**5a** (7:8 ratio, 30 %). Additionally, the vinyl-phosphirane complexes *anti*-**9** (δ^{31}P = – 157.1 ppm) and *syn*-**9** (δ^{31}P = – 150.2 ppm) were also produced in a 3:1 ratio (6 %). The vinyl-phosphiranes formed in this milder process (55 °C vs. 110 °C) corroborates the role of phosphabutadienes as reaction intermediates. Heating of isolated *anti*-**9** at 110 °C effected epimerization of the phosphorus center to give the *syn*-**9** isomer, which underwent the established [1,3]-sigmatropic shift[15] to phospholene complex **6**. The presumed reagent, the [PhP(Cl)W(CO)$_5$]-Cu-alkene complex,[14] is more sensitive than Ph-P=W(CO)$_5$ to steric congestion in the 1,2-cycloaddition, which is reflected in the lower yield of the 2-phosphabicyclobutanes **3a**. The competitive reaction is, in our opinion, the formation of zwitterion **7** for which there is computational support on related systems.[16] Compound **7** can also rearrange to phosphabutadiene **4a** in analogy to the addition of dichlorocarbene to cyclopropenes.[17] Ring closure then gives **5a**,[8] while two known hydride shifts[18] lead, via the secondary vinylphosphane complex **8**, to vinyl-phosphirane **9** (Scheme 3). The **4'**→**9'** process is exothermic by –1.8 kcal·mol^{-1} for the parent system (no phenyl substituent on the diene).[9]



Scheme 2. CuCl-catalyzed formation of **5a** and **9**.

Valence isomerization is sensitive to the nature of the bridgehead substituents, and this also applies to **3**→**4**→**5**. Reaction of cyclopropene **2b**, which has phenyl instead of methyl substituents, with the phosphinidene precursor **1** at 110 °C gave as sole products the 3-phosphacyclobutene complexes *cis*-**5b** (δ^{31}P = 43.8 ppm, ^{2}J(H,P) = 6.2 Hz) and *trans*-**5b** (δ^{31}P = 53.4 ppm, ^{2}J(H,P) = 9.6 Hz)[8] (5:1 ratio, 95 %); *cis*-**5b** was characterized by X-ray crystallography (Figure 4). Apparently, **3b** isomerizes faster than **3a**. In this case, phospholene **6** cannot be formed because the phenyl substituents render a hydride shift (to give **8**) impossible.

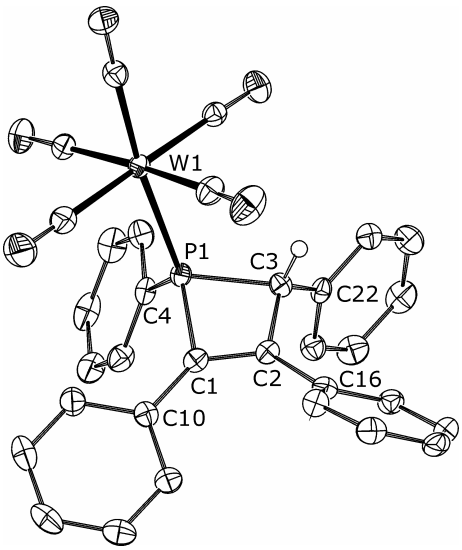


Figure 4. Displacement ellipsoid plot of *cis*-**5b** with ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å], angles and torsion angles [°]: W1-P1 2.4988(7), P1-C1 1.822(2), P1-C3 1.888(2), P1-C4 1.824(2), C1-C2 1.360(3), C1-C10 1.466(3), C2-C3 1.527(3), C2-C16 1.477(3), C3-C22 1.504(3); C1-P1-C3 75.93(11), P1-C1-C2 93.37(16), P1-C3-C2 85.66(14), C1-C2-C3 104.3(2); P1-C1-C2-C3 –7.26(18).

2-Phosphabicyclo[1.1.0]butanes *exo*-**3b** (δ^{31}P = – 70.5 ppm) and *endo*-**3b** (δ^{31}P = 3.8 ppm)[7] could be obtained (4:1 ratio, 33 %) by the milder CuCl-catalyzed reaction (2 equiv of **1**, 55 °C, 0.5 h). X-ray crystal structure of the *exo* isomer revealed two different triclinic polymorphs with Z=2 and Z=6, respectively, and very similar molecular structures (Figure 5). Polymorph I shows a folding angle (113.27(10)°) and a transannular bond length (1.510(2) Å) that are similar to those of *exo*-**3a**.

Heating of isolated **3b** (*exo* + *endo*, 4:1) in toluene at 50 °C for 60 h gave the favored phosphacyclobutene *cis*-**5b**, indicating that valence isomerization of the novel 2-phosphabicyclo[1.1.0]butanes is indeed directed by the bridgehead substituents (**3b** 50 °C; **3a** 130 °C). This behavior parallels that observed for the all-carbon analogue 2,2-dimethyl-bicyclo[1.1.0]butane, where the 1,3-diphenyl derivative isomerizes at 130 °C and the 1,3-dimethyl derivate at temperatures above 280 °C.[19]

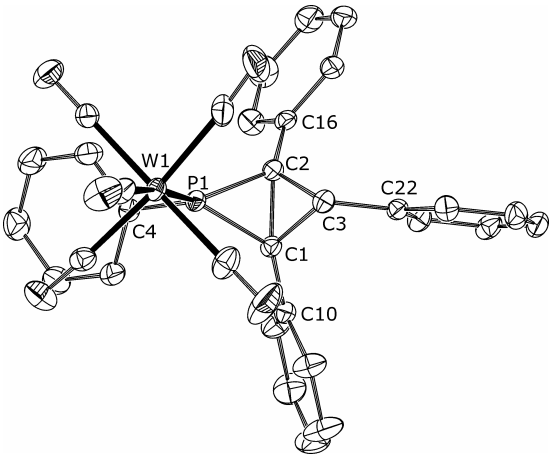


Figure 5. Displacement ellipsoid plot of *exo*-**3b** (polymorph I) with ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å], angles and torsion angles [°]: **polymorph I:** W1-P1 2.4688(4), P1-C1 1.8130(16), P1-C2 1.8286(16), P1-C4 1.8084(16), C1-C2 1.510(2), C1-C3 1.524(2), C1-C10 1.473(2), C2-C3 1.511(2), C2-C16 1.473(2), C3-C22 1.489(3); C1-P1-C2 48.98(7), P1-C1-C2 66.05(8), P1-C1-C3 96.18(10), C2-C1-C3 59.77(10), P1-C2-C1 64.97(8), P1-C2-C3 95.97(10), C1-C2-C3 60.57(10), C1-C3-C2 59.66(10), C1-C2-C16 141.37(14), C2-C1-C10 141.02(14); P1-C1-C2-C3 113.27(10). **polymorph II** (3 independent molecules): W1-P1 2.4640(9) [2.4605(9), 2.4682(9)], P1-C1 1.840(3) [1.822(3), 1.817(3)], P1-C2 1.815(3) [1.833(3), 1.836(3)], P1-C4 1.805(3) [1.797(3), 1.803(3)], C1-C2 1.507(4) [1.510(4)], C1-C3 1.515(4) [1.520(4)], C1-C10 1.469(4) [1.482(4)], C2-C3 1.518(4) [1.512(4), 1.512(4)], C2-C16 1.470(4) [1.471(4), 1.473(4)], C3-C22 1.494(4) [1.488(4), 1.494(4)]; C1-P1-C2 48.71(13) [48.79(13), 48.88(13)], P1-C1-C2 64.79(16) [65.99(16), 66.24(16)], P1-C1-C3 95.4(2) [96.77(19), 96.37(19)], C2-C1-C3 60.3(2) [59.9(2), 59.8(2)], P1-C2-C1 66.49(16) [65.22(16), 64.88(16)], P1-C2-C3 96.32(19) [96.61(19), 95.9(2)], C1-C2-C3 60.1(2) [60.4(2), 60.3(2)], C1-C3-C2 59.6(2) [59.7(2), 59.9(2)], C1-C2-C16 141.5(3) [140.2(3), 140.9(3)], C2-C1-C10 142.1(3) [140.6(3), 140.6(3)]; P1-C1-C2-C3 -112.87(19) [114.07(19), 113.38(19)].

6.5 Conclusion

$W(CO)_5$-complexed 2-phosphabicyclo[1.1.0]butanes are remarkably stable compounds that valence-isomerize to 3-phosphacyclobutenes via 1-phospha-butadienes at elevated temperatures. In contrast to the hydrocarbon analogues, the diene can be trapped as a phospholene due to rearrangements that are specific for the phosphorus compounds.

6.6 Computational Section

All density functional theory calculations (BP86) were performed with the Gaussian98 suite of programs,[9] using the LANL2DZ basis and pseudopotentials on tungsten, and the 6-31G* basis for all other atoms. The nature of the transition states was confirmed in each case with frequency calculations, and intrinsic reaction coordinate (IRC) calculations were performed to ascertain the connection between reactant and product.

6.7 Experimental Section

All experiments were performed under an atmosphere of dry nitrogen. Solids were dried *in vacuo*, and liquids were distilled (under N_2) prior to use. Solvents were used as purchased, except for toluene, which was distilled over sodium. NMR spectra were recorded (at 298K) on a Bruker Advance 250 (^{31}P; 85% H_3PO_4) and a MSL 400 (^1H, ^{13}C) and referenced internally to residual solvent resonances (^1H: δ 7.25 ppm ($CHCl_3$), $^{13}C\{^1H\}$: 77.0 ppm ($CDCl_3$). IR spectra were recorded on a Mattson-6030 Galaxy FT-IR spectrophotometer, and high-resolution mass spectra (HR-MS) was performed on a Finnigan Mat 900 mass spectrometer operating at an ionization potential of 70 eV. Melting points were measured on samples in unsealed capillaries and are uncorrected. CuCl (99 % purity) was purchased from Acros and stored under nitrogen before use. [5,6-Dimethyl-2,3-bis(methoxycarbonyl)-7-phenyl-7-phosphanorbornadiene] pentacarbonyltungsten **1**[20] and 1,2-dimethyl-3-phenylcyclopropene (**2a**)[6] were prepared according to literature procedures.

3a and **6**: **1** (591 mg, 0.90 mmol) and **2a** (156 mg, 1.08 mmol) were heated in refluxing toluene (3 mL) for 17 hours. Evaporation to dryness and chromatography of the residue over silica with pentane/toluene (9/1) as eluent gave *endo*-**3a** (155 mg, 30 %), *exo*-**3a** (200 mg, 39 %) both as colorless solids and **6** (20 mg, 4 %) as a pale yellow solid together with minor amounts of *cis*-**5a** (10 mg, 2 %) and *trans*-**5a** (5 mg, 1 %). Crystallization of *exo*- and *endo*-**3a** and **6** from pentane at – 20 °C afforded colorless crystals. *Exo*-**3a**: mp 115 – 116 °C; $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$): δ = – 85.1 (^1J(P,W) = 263.7 Hz); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 6.1 (d, ^2J(C,P) = 3.1 Hz; CH_3), 18.3 (d, ^1J(C,P) = 8.0 Hz; PCCH_3), 42.4 (d, ^2J(C,P) = 26.5

Hz; *C*H), 126.8 (s; *p*-PhCH), 128.4 (s; *m*-PhCH), 128.8 (d, ^3J(C,P) = 9.1 Hz; *m*-PhP), 129.2 (s; *o*-PhCH), 130.4 (d, ^4J(C,P) = 2.0 Hz; *p*-PhP), 132.0 (d, ^2J(C,P) = 11.1 Hz; *o*-PhP), 133.2 (d, ^1J(C,P) = 26.1 Hz; *ipso*-PhP), 134.7 (d, ^3J(C,P) = 23.5 Hz; *ipso*-PhCH), 195.8 (d, ^2J(C,P) = 8.3 Hz, ^1J(C,W) = 125.3 Hz; *cis*-CO), 197.8 (d, ^2J(C,P) = 31.0 Hz; *trans*-CO); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.67 (d, ^3J(H,P) = 8.0 Hz, 6H; C*H*$_3$), 2.03 (d, ^3J(H,P) = 26.5 Hz, 1H; C*H*), 7.12–7.15 (m, 2H; *o*-Ph*H*), 7.24–7.30 (m, 1H; *p*-Ph*H*), 7.34–7.38 (m, 2H; *m*-Ph*H*), 7.44–7.54 (m, 5H; PPh*H*); IR (KBr): ν = 1910, 1933, 1958 (s/br, CO_{eq}), 1979 (m, CO_{eq}), 2070 cm^{-1} (m, CO_{ax}). *Endo*-**3a**: mp 79–82 °C; ^{31}P{^{1}H} NMR (101.3 MHz, $CDCl_3$): δ = – 36.7 (^1J(P,W) = 260.3 Hz); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ = 7.4 (d, ^2J(C,P) = 9.1 Hz; *C*H$_3$), 27.8 (d, ^1J(C,P) = 9.7 Hz; P*C*CH$_3$), 49.1 (d, ^2J(C,P) = 7.2 Hz; *C*H), 126.9 (s; *p*-PhCH), 128.3 (s; *m*-PhCH), 128.5 (d, ^3J(C,P) = 9.4 Hz; *m*-PhP), 128.9 (s; *o*-PhCH), 130.4 (d, ^4J(C,P) = 1.9 Hz; *p*-PhP), 131.4 (d, ^2J(C,P) = 12.2 Hz; *o*-PhP), 131.9 (d, ^1J(C,P) = 19.6 Hz; *ipso*-PhP), 135.7 (d, ^3J(C,P) = 11.1 Hz; *ipso*-PhCH), 195.4 (d, ^2J(C,P) = 8.2 Hz, ^1J(C,W) = 125.0 Hz; *cis*-CO), 198.2 (d, ^2J(C,P) = 27.2 Hz, ^1J(C,W) = 147.3 Hz; *trans*-CO); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.76 (d, ^3J(H,P) = 11.9 Hz, 6H; C*H*$_3$), 2.48 (d, ^3J(H,P) = 23.0 Hz, 1H; C*H*), 7.02–7.05 (m, 2H; *o*-Ph*H*), 7.24–7.27 (m, 1H; *p*-Ph*H*), 7.26–7.34 (m, 2H; *m*-Ph*H*), 7.39–7.44 (m, 5H; PPh*H*); HR-MS (EI): *m/z* (%): 576 (9) [*M*]$^+$, 492 (36) [*M* – 3CO]$^+$, 464 (3) [*M* – 4CO]$^+$, 436 (44) [*M* – 5CO]$^+$; calcd for $C_{22}H_{17}O_5PW$: 576.0323, found: 576.0325; IR (KBr): ν = 1929 (s/br, CO_{eq}), 1991 (w, CO_{eq}), 2074 cm^{-1} (m, CO_{ax}). **6**: mp 107 °C; ^{31}P{^{1}H} NMR (101.3 MHz, $CDCl_3$): δ = 37.9 (^1J(P,W) = 240.4 Hz); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ = 17.7 (d, ^3J(C,P) = 4.7 Hz; *C*H$_3$), 36.2 (d, ^1J(C,P) = 23.7 Hz; *C*H$_2$), 61.1 (d, ^1J(C,P) = 19.0 Hz; Ph*C*H), 125.2 (d, ^2J(C,P) = 2.7 Hz; =*C*H), 127.8 (d, ^5J(C,P) = 3.5 Hz; *p*-PhCH), 128.7 (d, ^3J(C,P) = 8.7 Hz; *m*-PhP), 129.1 (d, ^2J(C,P) = 10.0 Hz; *o*-PhP), 129.1 (br. s; *o*-PhCH), 129.4 (d, ^4J(C,P) = 2.9 Hz; *m*-PhCH), 129.6 (d, ^4J(C,P) = 1.9 Hz; *p*-PhP), 137.5 (d, ^2J(C,P) = 5.8 Hz; *ipso*-PhCH), 138.9 (d, ^1J(C,P) = 32.0 Hz; *ipso*-PhP), 143.1 (d, ^2J(C,P) = 3.9 Hz; =*C*CH$_3$), 196.1 (d, ^2J(C,P) = 7.0 Hz, ^1J(C,W) = 125.6 Hz; *cis*-CO), 199.2 (d, ^2J(C,P) = 23.0 Hz; *trans*-CO); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.61 (d, ^4J(H,P) = 1.8 Hz, 3H; C*H*$_3$), 3.16–3.28 (m AB type, ^2J(H,P) = 6.7 Hz, 2H; C*H*$_2$), 3.98 (d, ^2J(H,P) = 7.2 Hz, 1H; Ph*CH*), 5.84 (dm, ^2J(H,P) = 17.5 Hz, 1H; =C*H*), 7.19–7.22 (m, 2H; *o*-Ph*H*), 7.28–7.33 (m, 1H; *p*-Ph*H*), 7.35–7.41 (m, 3H; *m*-Ph*H*, *p*-Ph*H*P), 7.44–7.49 (m, 2H; *m*-Ph*H*P), 7.54–7.59 (m, 2H; *o*-Ph*H*P); HR-MS (EI): *m/z* (%): 576 (30) [*M*]$^+$, 548 (16) [*M* – CO]$^+$, 492 (100) [*M* – 3CO]$^+$, 436 (76) [*M* – 5CO]$^+$; calcd for $C_{22}H_{17}O_5PW$: 576.0323, found: 576.03286; IR (KBr): ν = 1920 (s/br, CO_{eq}), 1991 (w, CO_{eq}), 2072 cm^{-1} (m, CO_{ax}).

Valence isomerization of *endo*-**3a**: *endo*-**3a** (128 mg, 0.22 mmol) was heated at 130 °C for 28 h in xylene (0.5 mL) generating *cis*-**5a** (28 %), *trans*-**5a** (7%), **6** (41 %), two unidentified products (δ^{31}P = 2.7, 3% and δ^{31}P = 36.2, 11%) together with unreacted *endo*-**3a** (2 %) (all NMR yields). Evaporation to dryness and flash chromatography of the residue over silica with pentane/toluene (9/1) as eluent gave the products (99 mg, 77 %) as a pale yellow oil.

3b: **2b** (122.6 mg, 0.46 mmol), **1** (598 mg, 0.91 mmol) and CuCl (10 mg, 0.1 mmol) were heated at 55 °C for 30 min in toluene (2 mL) and the reaction was stopped at incomplete conversion to ensure maximum yield of **3b**. Evaporation to dryness and chromatography of the residue over silica with pentane/toluene (9/1) as eluent gave a 4:1 isomeric mixture of *exo*-**3b** and *endo*-**3b** (107 mg, 33 %) as a pale yellow solid. Crystallization from pentane at – 20 °C afforded colorless crystals of *exo*-**3b**. *Exo*-**3b**: mp 124 °C (decomp.); $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$): δ = – 70.5 (^1J(P,W) = 262.0 Hz); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 31.0 (d, ^1J(C,P) = 3.0 Hz; PC*P*h), 44.1 (d, ^2J(C,P) = 27.2 Hz; *C*H), 126.6 (s; *p*-PhCH), 127.6 (d, ^5J(C,P) = 0.9 Hz; *m*-PhCH), 127.7 (s; *p*-PhC), 127.8 (d, ^3J(C,P) = 11.6 Hz; *m*-PhP), 128.4 (d, ^4J(C,P) = 0.9 Hz; *m*-PhC), 129.1 (s; *o*-PhCH), 129.7 (d, ^3J(C,P) = unresolved; *ipso*-PhCH), 129.8 (d, ^4J(C,P) = 4 Hz; *p*-PhP), 131.7 (d, ^3J(C,P) = 1.3 Hz; *o*-PhC), 132.0 (d, ^2J(C,P) = 10.1 Hz; *o*-PhP), 133.5 (d, ^{2}(C,P) = 22.1 Hz; *ipso*-PhC), 134.6 (d, ^1J(C,P) = 27.9 Hz; *ipso*-PhP), 195.6 (d, ^2J(C,P) = 8.0 Hz, ^1J(C,W) = 125.6 Hz; *cis*-CO), 197.7 (d, ^2J(C,P) = 32.7 Hz; *trans*-CO); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.79 (d, ^3J(H,P) = 28.7 Hz, 1H; C*H*), 6.74–6.78 (m, 2H; *o*-Ph*H*CH), 6.92–6.97 (m, 1H; *p*-Ph*H*CH), 6.97–7.02 (m, 2H; *m*-Ph*H*CH), 7.10–7.14 (m, 4H; *o*-Ph*H*), 7.18–7.25 (m, 6H; *m*-Ph*H*, *p*-Ph*H*), 7.28–7.33 (m, 2H; *o*-Ph*H*P), 7.38–7.47 (m, 2H, *m*-Ph*H*P), 7.62–7.65 (m, 1H, *p*-Ph*H*P); HR-MS (EI): *m/z* (%): 700 (22) $[M]^+$, 672 (3) $[M - CO]^+$, 616 (76) $[M - 3CO]^+$, 588 (6) $[M - 4CO]^+$, 560 (100) $[M - 5CO]^+$; calcd for $C_{32}H_{21}O_5PW$: 700.0636, found: 700.0634; IR (KBr): ν = 1929 (s/br, CO_{eq}), 1987 (w, CO_{eq}), 2070 cm^{-1} (m, CO_{ax}). *Endo*-**3b**: $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$): δ = 3.8 (^1J(P,W) = 271.8 Hz); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 5.08 (d, ^3J(H,P) = 31.3 Hz, 1H; C*H*), 6.82–7.47 (m, 20H).

5a and **9**: **1** (1.24 g, 1.90 mmol), **2a** (410 mg, 2.84 mmol) and CuCl (10 mg, 0.1 mmol) were heated at 55 °C for 15 h in toluene (8 mL). Evaporation to dryness and chromatography of the residue (black residue remains) over silica with pentane/toluene (9/1) as eluent gave *endo*-**3a** (40 mg, 4 %) as a colorless oil, *cis*-**5a** (160 mg, 14 %) as a colorless oil, *exo*-**3a** and *trans*-**5a** in a 10:8 ratio (310 mg, 28 %) as a colorless oil and *syn*- and *anti*-**9** in a 3:1 ratio (65 mg, 6 %) as a colorless oil. Crystallization of the mixture of *exo*-**3a** and *trans*-**5a** from pentane at – 80 °C afforded pale yellow crystals of *trans*-**5a**. *Syn*-**9** could be separated from *trans*-**9** by subsequential column chromatography and crystallization from pentane at – 80 °C. *Cis*-**5a**: $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$): δ = 46.3 (^1J(P,W) = 221.4 Hz); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 13.3 (d, ^2J(C,P) = 7.5 Hz; PCCH_3), 14.9 (d, ^3J(C,P) = 16.6 Hz; PC=CCH_3), 55.8 (d, ^1J(C,P) = 34.0 Hz; P*C*H), 126.5 (d, ^5J(C,P) = 3.2 Hz; *p*-PhCH), 127.5 (d, ^3J(C,P) = 4.1 Hz; *o*-PhCH), 127.9 (d, ^3J(C,P) = 9.3 Hz; *m*-PhP), 128.2 (d, ^4J(C,P) = 2.8 Hz; *m*-PhCH), 129.6 (d, ^4J(C,P) = 2.2 Hz; *p*-PhP), 130.6 (d, ^2J(C,P) = 10.4 Hz; *o*-PhP), 135.2 (d, ^2J(C,P) = 8.0 Hz; *ipso*-PhCH), 135.1 (d, ^1J(C,P) = 24.2 Hz; *ipso*-PhP), 138.9 (d, ^1J(C,P) = 40.4 Hz; P*C*=), 149.5 (d, ^2J(C,P) = 5.9 Hz; PC=*C*), 196.6 (d, ^2J(C,P) = 7.0 Hz, ^1J(C,W) = 125.2 Hz; *cis*-CO), 199.8 (d, ^2J(C,P) = 21.6 Hz, ^1J(C,W) = 145.8 Hz; *trans*-CO); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.83 (m, ^5J(H,H) = 1.1 Hz, 3H; PC=CCH_3), 2.16 (dm, ^3J(H,P) = 13.0 Hz, ^5J(H,H) = 1.1 Hz, 3H; PCCH_3),

4.38 (m, 1H; C*H*), 6.75–6.79 (m, 2H; *o*-Ph*H*CH), 6.96–7.03 (m, 5H; *m*-Ph*H*CH, *p*-Ph*H*CH, *o*-Ph*H*P), 7.10–7.17 (m, 3H; *m*-Ph*H*P, *p*-Ph*H*P). *Trans*-**5a**: mp 111 °C; $^{31}P\{^{1}H\}$ NMR (101.3 MHz, $CDCl_3$): δ = 55.2 (^{1}J(P,W) = 237.5 Hz); $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 12.6 (d, ^{2}J(C,P) = 7.4 Hz; PC*C*H$_3$), 15.0 (d, ^{3}J(C,P) = 15.6 Hz; PC=C*C*H$_3$), 54.2 (d, ^{1}J(C,P) = 32.4 Hz; P*C*H), 127.7 (d, ^{5}J(C,P) = 4.3 Hz; *p*-PhCH), 128.5 (d, ^{3}J(C,P) = 5.3 Hz; *o*-PhCH), 128.7 (d, ^{3}J(C,P) = 8.6 Hz; *m*-PhP), 129.0 (d, ^{2}J(C,P) = 10.5 Hz; *o*-PhP), 129.1 (d, ^{4}J(C,P) = 3.7 Hz; *m*-PhCH), 129.8 (d, ^{4}J(C,P) = 2.1 Hz; *p*-PhP), 136.6 (d, ^{2}J(C,P) = 4.7 Hz; *ipso*-PhCH), 139.3 (d, ^{1}J(C,P) = 40.3 Hz; P*C*=), 140.7 (d, ^{1}J(C,P) = 17.4 Hz; *ipso*-PhP), 148.2 (d, ^{2}J(C,P) = 4.0 Hz; PC=*C*), 195.8 (d, ^{2}J(C,P) = 7.1 Hz, ^{1}J(C,W) = 125.2 Hz; *cis*-CO), 199.1 (d, ^{2}J(C,P) = 23.6 Hz; *trans*-CO); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.81 (m, ^{5}J(H,H) = 1.2 Hz, 3H; PC=CC*H*$_3$), 2.12 (dm, ^{3}J(H,P) = 12.5 Hz, ^{5}J(H,H) = 1.2 Hz, 3H; PCC*H*$_3$), 3.94 (dm, ^{2}J(H,P) = 9.5 Hz, 1H; C*H*), 7.17–7.20 (m, 2H; *o*-Ph*H*CH), 7.29–7.43 (m, 4H; *m*-Ph*H*CH, *p*-Ph*H*CH, *p*-Ph*H*P), 7.46–7.57 (m, 4H; *m*-Ph*H*P, *o*-Ph*H*P); HR-MS (EI): *m/z* (%): 576 (39) $[M]^+$, 548 (3) $[M - CO]^+$, 492 (94) $[M - 3CO]^+$, 464 (10) $[M - 4CO]^+$, 436 (100) $[M - 5CO]^+$; calcd for $C_{22}H_{17}O_5PW$: 576.0323, found: 576.0318; IR (KBr): ν = 1929 (s/br, CO_{eq}), 1987 (m, CO_{eq}), 2068 cm^{-1} (m, CO_{ax}). *Syn*-**9**: $^{31}P\{^{1}H\}$ NMR (101.3 MHz, $CDCl_3$): δ = – 157.1 (^{1}J(P,W) = 255.2 Hz); $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 13.1 (d, ^{1}J(C,P) = 11.0 Hz; P*C*H$_2$), 19.6 (d, ^{3}J(C,P) = 1.7 Hz; *C*H$_3$), 35.7 (d, ^{1}J(C,P) = 18.1 Hz; P*C*H), 125.6 (d, ^{3}J(C,P) = 7.4 Hz; =*C*H), 126.3 (s; *p*-Ph), 128.0 (s; *m*-Ph), 128.4 (d, ^{3}J(C,P) = 10.1 Hz; *m*-PhP), 128.5 (d, ^{5}J(C,P) = 2.1 Hz; *o*-Ph), 130.4 (d, ^{4}J(C,P) = 2.2 Hz; *p*-PhP), 130.7 (d, ^{1}J(C,P) = 30.0 Hz; *ipso*-PhP), 131.2 (d, ^{2}J(C,P) = 4.0 Hz; =*C*CH$_3$), 132.8 (d, ^{2}J(C,P) = 12.0 Hz; *o*-PhP), 137.1 (d, ^{4}J(C,P) = 2.7 Hz; *ipso*-PhC), 195.7 (d, ^{2}J(C,P) = 8.3 Hz, ^{1}J(C,W) = 125.6 Hz; *cis*-CO), 198.1 (d, ^{2}J(C,P) = 31.0 Hz; *trans*-CO); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.74 (m, ^{2}J(H,P) = 1.4 Hz, ^{2}J(H,H) = 9.0 Hz, 1H; PC*H*$_2$), 1.81 (s, 3H; C*H*$_3$), 2.40 (m, ^{2}J(H,P) = 7.6 Hz, ^{2}J(H,H) = 9.0 Hz, 1H; PC*H*$_2$), 2.51 (m, 1H; P*C*H), 5.91 (m, 1H; =C*H*), 6.69 (m, 2H; *o*-Ph*H*), 7.10–7.19 (m, 3H; *m*-Ph*H*, *p*-Ph*H*), 7.29–7.42 (m, 5H; Ph*H*P); HR-MS (EI): *m/z* (%): 576 (20) $[M]^+$, 548 (12) $[M - CO]^+$, 492 (100) $[M - 3CO]^+$, 436 (80) $[M - 5CO]^+$; calcd for $C_{22}H_{17}O_5PW$: 576.0323, found: 576.03184. *Anti*-**9**: $^{31}P\{^{1}H\}$ NMR (101.3 MHz, $CDCl_3$): δ = – 150.2 (^{1}J(P,W) = 263.3 Hz); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.90–1.97 (m, 1H; C*H*), 2.14–2.19 (m, 1H; C*H*), 2.21 (s, 3H; C*H*$_3$), 2.59–2.67 (m, 1H; C*H*), 6.25 (m, 1H; =C*H*), 7.06–7.09 (m, 2H; *o*-Ph*H*), 7.20–7.40 (m, 3H; *m*-Ph*H*, *p*-Ph*H*), 7.40–7.45 (m, 3H; *m*-Ph*H*P, *p*-Ph*H*P), 7.53–7.60 (m, 2H; *o*-Ph*H*P).

5b: **1** (261 mg, 0.40 mmol), **2b** (118 mg, 0.44 mmol) and CuCl (10 mg, 0.1 mmol) were heated at 55 °C for 38 h in toluene (2 mL). Evaporation to dryness and chromatography of the residue over silica with pentane/toluene (4/1) as eluent gave *cis*-**5b** (215 mg, 77 %) as a pale yellow solid together with a trace of *trans*-**5b** (~2%). Crystallization from pentane at – 20 °C afforded colorless crystals of *cis*-**5b**: mp 117–118 °C; $^{31}P\{^{1}H\}$ NMR (101.3 MHz, $CDCl_3$): δ = 43.8 (^{1}J(P,W) = 230.9 Hz); $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 53.7 (d, ^{1}J(C,P) = 35.7 Hz; P*C*H), 126.3 (d, ^{4}J(C,P) = 3.2 Hz; *m*-PhCH), 127.9 (d, ^{4}J(C,P) = 0.8 Hz; *o*-PhC=CP), 127.9 (d, ^{3}J(C,P)

= 4.0 Hz; *o*-PhCH), 128.0 (d, ^3J(C,P) = 9.7 Hz; *m*-PhP), 128.1 (d, ^5J(C,P) = 2.8 Hz; *p*-PhCH), 128.7 (s; *m*-PhC=CP), 128.7 (d, ^3J(C,P) = 6.1 Hz; *o*-Ph(C=)P), 128.9 (s; *m*-Ph(C=)P), 129.2 (d, ^5J(C,P) = 1.2 Hz; *p*-Ph(C=)P), 129.5 (s; *p*-PhC=CP), 130.2 (d, ^4J(C,P) = 2.3 Hz; *p*-PhP), 132.1 (d, ^2J(C,P) = 11.3 Hz; *o*-PhP), 133.5 (d, ^2J(C,P) = 6.6 Hz; *ipso*-Ph(C=)P), 134.3 (d, ^1J(C,P) = 24.4 Hz; *ipso*-PhP), 134.3 (d, ^3J(C,P)= 17.5 Hz; *ipso*-PhC=CP), 134.9 (d, ^2J(C,P) = 7.9 Hz; *ipso*-PhCH), 139.0 (d, ^1J(C,P) = 38.9 Hz; P*C*=), 148.2 (d, ^2J(C,P) = 4.6 Hz; PC=*C*), 196.3 (d, ^2J(C,P) = 6.9 Hz, ^1J(C,W) = 125.1 Hz; *cis*-CO), 198.9 (d, ^2J(C,P) = 22.9 Hz, ^1J(C,W) = 144.7 Hz; *trans*-CO); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 5.09 (d, ^2J(H,P) = 6.2 Hz, 1H; PC*H*), 6.80–6.82 (m, 2H; *o*-Ph*H*CH), 6.90–6.92 (m, 3H; *m*-Ph*H*CH, *p*-Ph*H*CH), 7.16–7.25 (m, 3H; *m*-Ph*H*P, *p*-Ph*H*P), 7.25–7.30 (m, 3H; *m*-Ph*H*C=CP, *p*-Ph*H*C=CP), 7.35–7.40 (m, 5H; *m*-Ph*H*(C=)P, *p*-Ph*H*(C=)P, *o*-Ph*H*P), 7.50–7.52 (m, 2H; *o*-Ph*H*C=CP), 7.61–7.64 (m, 2H; *o*-Ph*H*(C=)P); HR-MS (EI): *m/z* (%): 700 (23) $[M]^+$, 672 (2) $[M - CO]^+$, 616 (56) $[M - 3CO]^+$, 588 (3) $[M - 4CO]^+$, 560 (66) $[M - 5CO]^+$; calcd for $C_{32}H_{21}O_5PW$: 700.0636, found: 700.06486; IR (KBr): ν = 1921 (s/br, CO_{eq}), 1979 (w, CO_{eq}), 2070 cm^{-1} (m, CO_{ax}). Or **5b**: **1** (294 mg, 0.45 mmol) and **2b** (133 mg, 0.49 mmol) were heated in refluxing toluene (2 mL) for 16 hours. Evaporation to dryness and chromatography of the residue over silica with pentane/toluene (4/1) as eluent gave a 5:1 isomeric mixture of *cis*-**5b** and *trans*-**5b** (300 mg, 95 %) as a pale yellow oil. Crystallization from pentane at –20 °C afforded colorless crystals of *cis*-**5b** together with a 1:3 isomeric mixture of *cis*-**5b** and *trans*-**5b**. *Trans*-**5b**: ^{31}P{^{1}H} NMR (101.3 MHz, $CDCl_3$): δ = 53.4 (^1J(P,W) = 247.0 Hz); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 4.60 (d, ^2J(H,P) = 9.6 Hz, 1H; PC*H*), 7.10–7.70 (m, 20H; Ph*H*).

Crystal structure determinations: X-ray intensities were measured on a Nonius KappaCCD diffractometer with rotating anode (graphite monochromator, Mo-K_α, λ = 0.71073 Å) at a temperature of 150 K. The structures were solved with automated Patterson methods with the program DIRDIF99[21] and refined with the program SHELXL97[22] against F^2 of all reflections. The drawings, geometry calculations, and checking for higher symmetry was performed with the program PLATON.[23]

Compound *exo*-3a. $C_{22}H_{17}O_5PW$, Fw = 576.18, colourless needle, 0.60 × 0.09 × 0.09 mm^3. Monoclinic crystal system, space group $P2_1/c$ (no. 14). Cell parameters: a = 6.8439(1), b = 21.3415(2), c = 14.4400(1) Å, β = 95.2844(3)°, V = 2100.13(4) $Å^3$. Z = 4, ρ = 1.822 g/cm^3. 37092 reflections were measured up to $(\sin\theta/\lambda)_{max}$ = 0.65 $Å^{-1}$. An absorption correction based on multiple measured reflections was applied (μ = 5.61 mm^{-1}, 0.53-0.61 correction range). 4805 reflections were unique (R_{int} = 0.048). Non hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in the difference Fourier map. Hydrogen atom H3 was refined freely with isotropic displacement parameters, all other hydrogen atoms were refined as rigid groups. 268 refined parameters, no restraints. R [$I > 2\sigma(I)$]: R1 = 0.0178, wR2 = 0.0406. R [all refl.]: R1 = 0.0219, wR2 = 0.0423. GoF = 1.065. Residual electron density between –0.84 and 1.06 e/$Å^3$.

Compound *endo*-3a. $C_{22}H_{17}O_5PW$, Fw = 576.18, colourless block, 0.30 × 0.15 × 0.06 mm^3. Monoclinic crystal system, space group $P2_1/c$ (no. 14). Cell parameters: a = 8.2108(1), b = 15.0945(1), c = 17.8628(2) Å, β = 99.0907(3)°, V = 2186.07(4) Å^3. Z = 4, ρ = 1.751 g/cm^3. 53784 reflections were measured up to $(\sin\theta/\lambda)_{max}$ = 0.65 Å^{-1}. An analytical absorption correction was applied (μ = 5.39 mm^{-1}, 0.23-0.73 correction range). 5010 reflections were unique (R_{int} = 0.046). Non hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in the difference Fourier map. Hydrogen atom H3 was refined freely with isotropic displacement parameters, all other hydrogen atoms were refined as rigid groups. 268 refined parameters, no restraints. R [I > 2σ(I)]: R1 = 0.0175, wR2 = 0.0403. R [all refl.]: R1 = 0.0222, wR2 = 0.0423. GoF = 1.071. Residual electron density between –0.63 and 1.51 e/Å^3.

Compound 6. $C_{22}H_{17}O_5PW$, Fw = 576.18, colourless needle, 0.39 × 0.18 × 0.12 mm^3. Monoclinic crystal system, space group C2/c (no. 15). Cell parameters: a = 37.996(3), b = 8.9553(4), c = 26.4314(15) Å, β = 110.813(5)°, V = 8406.9(9) Å^3. Z = 16, ρ = 1.821 g/cm^3. 42631 reflections were measured up to $(\sin\theta/\lambda)_{max}$ = 0.65 Å^{-1}. An analytical absorption correction was applied (μ = 5.60 mm^{-1}, 0.29-0.62 correction range). 9640 reflections were unique (R_{int} = 0.037). Non hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in the difference Fourier map and were refined as rigid groups. 525 refined parameters, no restraints. R [I > 2σ(I)]: R1 = 0.0213, wR2 = 0.0462. R [all refl.]: R1 = 0.0378, wR2 = 0.0515. GoF = 1.104. Residual electron density between –1.20 and 2.05 e/Å^3.

Compound *cis*-5b. $C_{32}H_{21}O_5PW$, Fw = 700.31, colourless plate, 0.42 × 0.36 × 0.12 mm^3. Monoclinic crystal system, space group $P2_1/c$ (no. 14). Cell parameters: a = 10.9428(1), b = 22.9359(2), c = 15.0824(1) Å, β = 133.2674(4)°, V = 2756.40(4) Å^3. Z = 4, ρ = 1.688 g/cm^3. 32271 reflections were measured up to $(\sin\theta/\lambda)_{max}$ = 0.65 Å^{-1}. An analytical absorption correction was applied (μ = 4.29 mm^{-1}, 0.33-0.70 correction range). 6296 reflections were unique (R_{int} = 0.039). Non hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in the difference Fourier map. Hydrogen atom H3 was refined freely with isotropic displacement parameters, all other hydrogen atoms were refined as rigid groups. 356 refined parameters, no restraints. R [I > 2σ(I)]: R1 = 0.0192, wR2 = 0.0474. R [all refl.]: R1 = 0.0227, wR2 = 0.0489. GoF = 1.077. Residual electron density between –0.79 and 1.21 e/Å^3.

Compound *exo*-3b (polymorph I). $C_{32}H_{21}O_5PW$, Fw = 700.31, colourless needle, 0.48 × 0.27 × 0.09 mm^3. Triclinic crystal system, space group $P\overline{1}$ (no. 2). Cell parameters: a = 10.4005(8), b = 10.7789(8), c = 14.4436(12) Å, α = 83.618(6), β = 78.886(6), γ = 61.670(5)°, V = 1398.2(2) Å^3. Z = 2, ρ = 1.663 g/cm^3. 33814 reflections were measured up to $(\sin\theta/\lambda)_{max}$ = 0.70 Å^{-1}. An absorption correction based on multiple measured reflections was applied (μ = 4.23 mm^{-1}, 0.31-0.68 correction range). 8122 reflections were unique (R_{int} = 0.025). Non hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were

located in the difference Fourier map. Hydrogen atom H3 was refined freely with isotropic displacement parameters, all other hydrogen atoms were refined as rigid groups. 356 refined parameters, no restraints. R [$I > 2\sigma(I)$]: R1 = 0.0163, wR2 = 0.0332. R [all refl.]: R1 = 0.0221, wR2 = 0.0345. GoF = 1.034. Residual electron density between –0.63 and 0.79 e/Å^3.

Compound *exo*-3b (polymorph II). $C_{32}H_{21}O_5PW$, Fw = 700.31, colourless block, 0.24 × 0.18 × 0.12 mm^3. Triclinic crystal system, space group $P\overline{1}$ (no. 2). Cell parameters: a = 10.4176(8), b = 17.1058(17), c = 23.9196(19) Å, α = 96.436(6), β = 92.693(7), γ = 97.143(8)°, V = 4194.7(6) Å^3. Z = 6, ρ = 1.663 g/cm^3. 65484 reflections were measured up to $(\sin\theta/\lambda)_{max}$ = 0.61 Å^{-1}. An absorption correction based on multiple measured reflections was applied (μ = 4.23 mm^{-1}, 0.45-0.60 correction range). 15630 reflections were unique (R_{int} = 0.031). Non hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in the difference Fourier map. Hydrogen atom H13, H23, and H33 were kept fixed at their located position, all other hydrogen atoms were refined as rigid groups. 356 refined parameters, no restraints. R [$I > 2\sigma(I)$]: R1 = 0.0246, wR2 = 0.0444. R [all refl.]: R1 = 0.0467, wR2 = 0.0491. GoF = 1.024. Residual electron density between –0.50 and 1.79 e/Å^3.

CCDC 275002 (***exo*-3a)**, 275003 (***endo*-3a**), 275004 (**6**), 275005 (***cis*-5b**), 275006 (***exo*-3b**, polymorph I), and 275007 (***exo*-3b**, polymorph II) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

6.8 References and Notes

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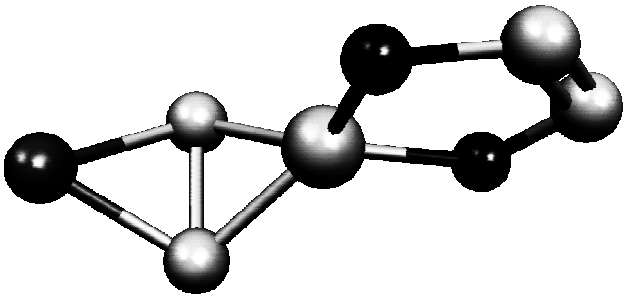
2-Phospha-4-silabicyclo[1.1.0]butane as a Reactive Intermediate

7

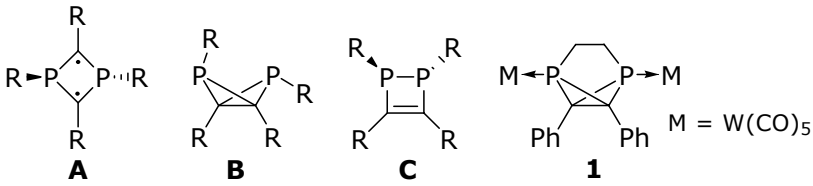
The thermally stable silylene Si[$(NCH_2{}^tBu)_2C_6H_4$-1,2] reacts with 1*H*-phosphirenes to give the first isolated 2,3-dihydro-1,3-phosphasiletes, a unique type of zwitterion, and 1,2-dihydro-1,2-phosphasiletes. The novel 2-phospha-4-silabicyclo[1.1.0]butane (see picture) is a reactive intermediate in the reaction, whose course can be tuned by changing the substituents.



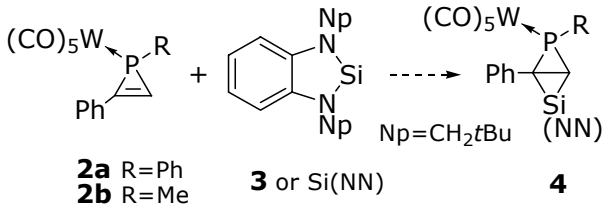
Published in: *Angew. Chem.* **2004**, *116*, 3556–3559; *Angew. Chem. Int. Ed.* **2004**, *43*, 3474–3477.

7.1 Introduction

Bicyclo[1.1.0]butane remains a fascinating compound. Stretching of its central C–C σ-bond culminates in a planar singlet diradical transition structure for inversion,[1] whereas stretching of the peripheral bonds leads to valence isomerization.[2] Bridging heteroatoms affect both processes. They enable the coexistence of the puckered bicyclic and planar diyl structures, and have thereby sparked intense studies dominated by recent discoveries of diphosphorus analogues. Niecke et al. synthesized a crystalline 2,4-diphosphacyclobutane-1,3-diyl **A**[3] that isomerizes photolytically to 2,4-diphosphabicyclo[1.1.0]butane **B**[4] and thermally to 1,2-dihydro-1,2-diphosphete **C**.[5] A still more congested diyl **A** that does not isomerize was reported by Yoshifuji and co-workers.[6] The group of Bertrand obtained both stable planar diyl and puckered forms for the isoelectronic 1,3-dibora-2,4-diphosphoniocyclobutanes.[7] 2,4-Diphospha-bicyclo[1.1.0]butane is puckered when the phosphorus atoms are *endo*,*endo* substituted as in dihydro-diphosphabenzvalene **1**, which Mathey and co-workers obtained by an *intra*molecular phosphinidene addition to the C=C bond of a 1*H*-phosphirene.[8] Without geometrical constraints, such additions invariably lead to 1,2-diphosphetes of type **C** by isomerization or direct CP insertion.[9]

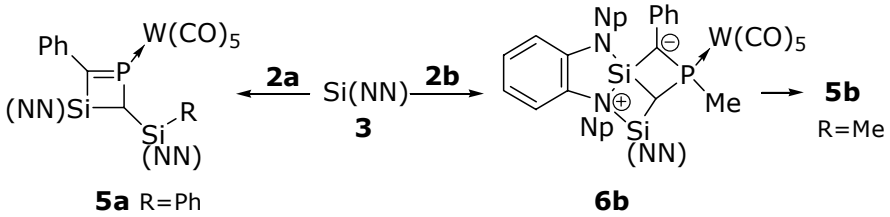


Data on 2,4-disilabicyclo[1.1.0]butanes[10] is limited to two disilabenzvalenes[11] and is absent for the corresponding planar diyls. Only a single 2-silabenzvalene is known, generated by photolysis of a silabenzene.[12] For the synthesis of the 2,4-disila derivatives Ando et al. applied valence isomerization of bis(silirene), which involves an intramolecular silylene addition to the C=C bond of a silirene.[11] The use of stable silylenes might simplify this approach to a broader array of hetero derivatives, which we decided to explore for the unknown 2-phospha-4-silabicyclo[1.1.0]butanes **4**.



7.2 Synthesis of 2,3-Dihydro-1,3-phosphasiletes

Reaction of silylene Si[(NCH$_2$^{t}Bu)$_2$C$_6$H$_4$-1,2] **3**[13] with 1*H*-phosphirene **2a**[14] in *n*-hexane at room temperature results in red crystalline 2,3-dihydro-1,3-phosphasilete **5a** instead of the desired **4** (Scheme 1).[15] Evidently, two silylenes are involved, one in forming the novel ring structure and the other as a substituent after transfer of a phenyl group. No intermediate was detected by ^{31}P NMR spectroscopy, either at low temperatures or with different stoichiometries of the reactants. The W(CO)$_5$-complexed phosphaalkene part of **5a** is characterized by the downfield absorptions at δ^{31}P = 278.3 ppm (^1J(P,W) = 254.0 Hz) and δ^{13}C = 197.3 ppm (^1J(C,P) = 3.5 Hz). A single-crystal X-ray analysis confirmed the structure of **5a** (Figure 1).[16] Its four membered ring deviates from planarity owing to steric congestion, which is reflected in the torsion angle of 11.6(2)° for C1-P1-C2-Si1. The P1–C1 and P1–C2 bond lengths (1.689(4) and 1.835(4) Å) are normal, but the short Si1–C1 bond (1.841(5) Å) suggest some delocalization of charge.



Scheme 1. Synthesis of 2,3-dihydro-1,3-phosphasiletes **5**.

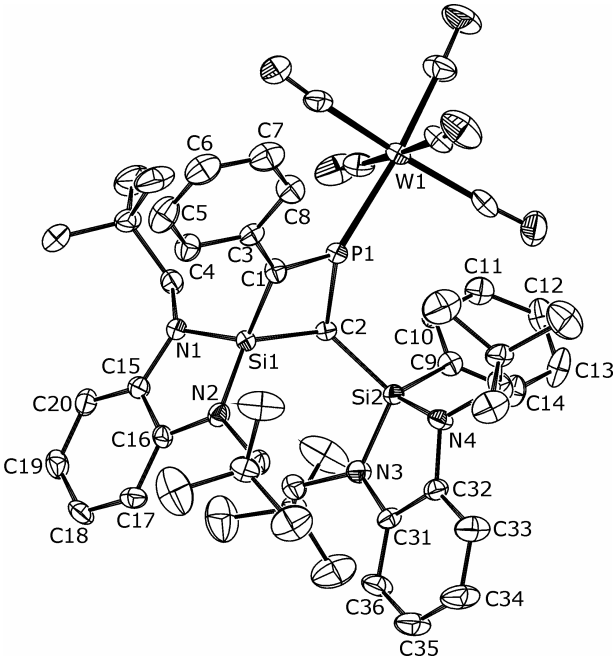


Figure 1. Structure of **5a** in the crystal (displacement ellipsoids drawn at the 50% probability level; hydrogen atoms and the hexane solvent molecule are omitted for clarity). Selected bond lengths [Å], angles and torsion angles [°]: W1-P1 2.4492(11), P1-C1 1.689(4), P1-C2 1.835(4), Si1-C1 1.841(5), Si1-C2 1.908(4); C1-P1-C2 92.9(2), P1-C2-Si1 86.13(17), C1-Si1-C2 85.96(18), P1-C1-Si1 92.7(2); C1-P1-C2-Si1 11.6(2).

To lower the migratory aptitude of the phosphorus substituent, we replaced the phenyl for a methyl group and used 1*H*-phosphirene **2b**,[14] instead of **2a**, for the addition of silylene **3**. This had the desired effect, giving the crystalline zwitterion **6b** (68%), which only rearranged at elevated temperatures (75 °C, 2 h) to 2,3-dihydro-1,3-phosphasilete **5b** (Scheme 1). The molecular structure of **6b** (Figure 2,[16] the crystal contains two independent molecules with similar geometries) shows a unique fused tricyclic ring structure which is retained in solution (δ^{31}P = – 6.8 ppm (^1J(P,W) = 240.0 Hz), δ^{29}Si = – 11.2 (^2J(Si,P) = 17.2 Hz, SiNN) and – 33.4 ppm (^2J(Si,P) = 18.4 Hz, SiNN$^+$). The negatively charged C1 is in a planar environment and is surrounded by shortened C1–P1 (1.793(4) Å), C1–C4 (1.455(6) Å) and C1–Si1 (1.750(4) Å) bonds that can be attributed to negative hyperconjugation, which is supported by the shielding of the silicon atom Si1 (δ^{29}Si = – 33.4 ppm).[17]

Furthermore, the cationic N2 lengthens the N2–Si and N2–C bonds.[18]

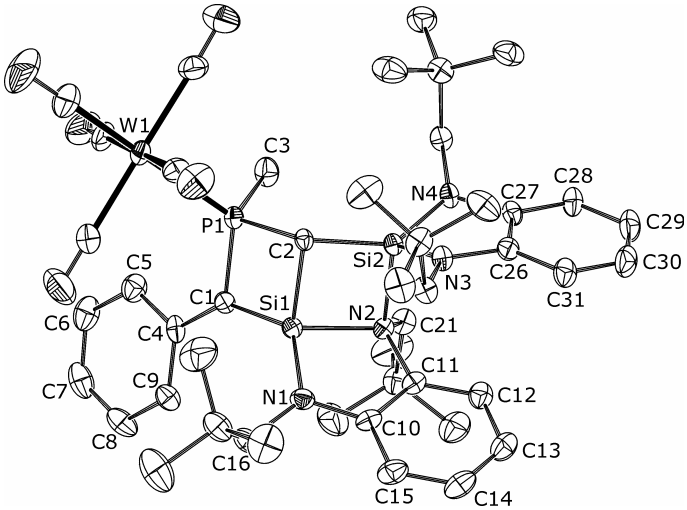
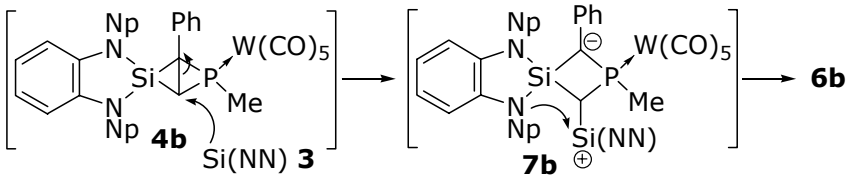


Figure 2. Structure of **6b** in the crystal, one of the two crystallographically independent molecules is shown (displacement ellipsoids drawn at the 50% probability level; hydrogen atoms omitted for clarity). Selected bond lengths [Å], angles and torsion angles [°]: W1-P1 2.5363(12), P1-C1 1.793(4), P1-C2 1.863(4), Si1-N1 1.725(4), Si1-N2 1.923(4), Si1-C1 1.750(4), Si1-C2 1.906(4), Si2-N2 1.933(4), Si2-N3 1.710(4), Si2-N4 1.705(4), Si2-C2 1.828(4), N1-C10 1.409(6), N1-C16 1.471(6), N2-C11 1.471(5), N2-C21 1.510(5), C1-C4 1.455(6); C1-P1-C2 90.79(19), P1-C2-Si1 85.70(18), C1-Si1-C2 90.70(19), P1-C1-Si1 92.7(2); C2-P1-C1-Si1 – 2.4(2), P1-C1-C4-C5 8.2(8).

7.3 Mechanism

We assume that the reaction starts by addition of the silylene to the C=C bond of the phosphirene to give 2-phospha-4-silabicyclo[1.1.0]butane **4b** as a transient intermediate, followed by attack of a second silylene to the bridgehead carbon in a manner analogous to the reaction of nucleophiles with bicyclo[1.1.0]butane (Scheme 2).[19] The resulting **7b** carries a silylium cation, which requires stabilization[20] by coordination with the lone pair of electrons of a nearby nitrogen atom.[21]



Scheme 2. Mechanism for the formation of zwitterion **6b**.

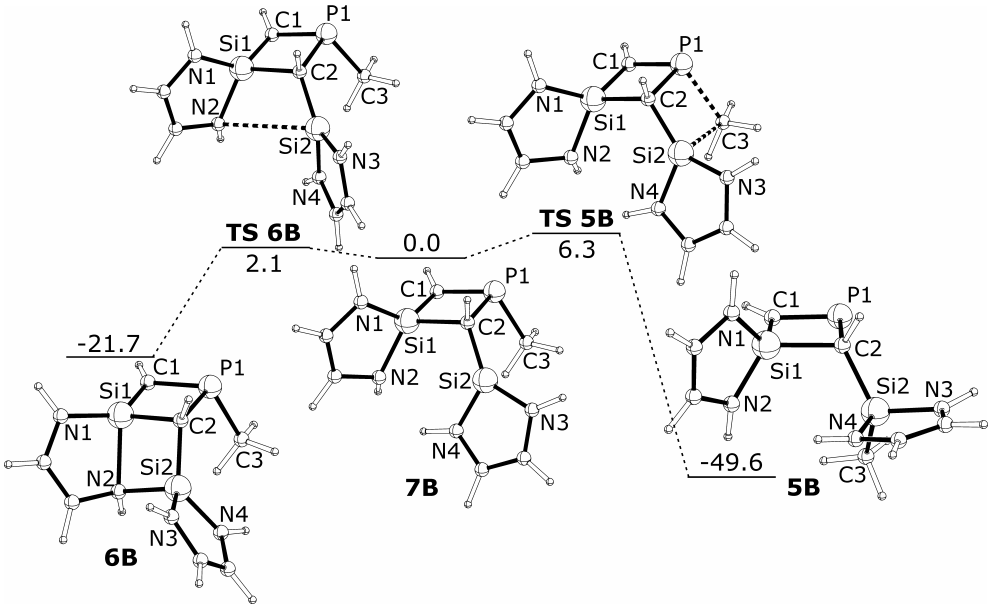
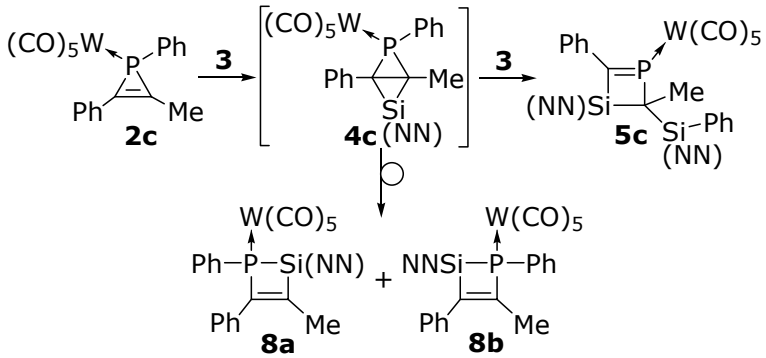


Figure 3. Relative SCS-MP2/6-311+G**//B3YLP/6-31G* energies (in kcal·mol^{-1}) for the rearrangement of **6B** to the thermodynamic more stable **5B** with selected bond lengths [Å], angles and torsion angles [°] of **5B**: P1-C1 1.693, P1-C2 1.894, Si1-C1 1.866, Si1-C2 1.910, C1-P1-C2 90.6, P1-C2-Si1 88.2, C1-Si1-C2 85.1, P1-C1-Si1 96.0, C1-P1-C2-Si1 –1.0; **TS5B**: P1-C1 1.754, P1-C2 1.909, P1-C3 2.111, Si1-C1 1.777, Si1-C2 1.959, Si2-C3 2.504; **6B**: P1-C1 1.835, P1-C2 1.942, P1-C3 1.894, Si1-N1 1.760, Si1-N2 2.066, Si1-C1 1.718, Si1-C2 1.897, Si2-N2 1.894, Si2-N3 1.735, Si2-N4 1.738, Si2-C2 1.849, C1-P1-C2 88.2, P1-C2-Si1 84.9, C1-Si1-C2 93.2, P1-C1-Si1 93.6, C2-P1-C1-Si1 –3.3; **TS6B**: P1-C1 1.797, P1-C2 1.930, P1-C3 1.901, Si1-C1 1.750, Si1-C2 2.000, Si2-N2 3.328, Si2-C3 3.289; **7B**: P1-C1 1.795, P1-C2 1.937, P1-C3 1.905, Si1-C1 1.751, Si1-C2 1.992, Si2-N2 3.401, Si2-C3 3.167.

This hypothesis was tested with SCS-MP2/6-311+G** energy calculations on B3LYP/6-31G* optimized model structures (labeled **B**)[22] which are devoid of

$W(CO)_5$, carry H instead of Np substituents, and have the nitrogens linked by ethylene instead of phenyl groups. This simplification is validated by the similarity in optimized structures between **4B** and that containing the Np and $W(CO)_5$ groups. Formation of **4B** from the reactants $C_2H_4N_2Si$ and C_3H_5P is exothermic by 17.5 kcal·mol^{-1} with an additional 8.5 kcal·mol^{-1} for the addition of a second silylene to give **7B** (Figure 3). Lewis base stabilization of the silylium cation gives the kinetically favored zwitterion **6B** (ΔE = 21.7; $\Delta E^{\ddagger}$ = 2.1 kcal·mol^{-1}), whereas a 1,3-methyl shift from phosphorus to silicon results in the thermodynamically favored phosphasilete **5B** (ΔE = 49.6; $\Delta E^{\ddagger}$ = 6.3 kcal·mol^{-1}). Such 1,3-shifts to an electron deficient silicon are very rare for both the methyl and phenyl groups.[23,24]



Scheme 3. Valence isomerization of **4c**.

7.4 Valence Isomerization

To reduce the attractiveness of the transient 2-phospha-4-silabicyclo[1.1.0]butane for attack by a second silylene, a methyl group was introduced at the bridgehead position by treating 1*H*-phosphirene **2c**[14] with **3**. Although this had the desired effect, mainly valence isomerization occurred, because of the elevated temperatures (80 °C, 13 h) required for the reaction, resulting in the isomeric 1,2-dihydro-1,2-phosphasiletes **8a** and **8b**,[25] together with the formation of some **5c** (5:2:2; Scheme 3). After fractional crystallization, **8a** could be obtained as a yellow solid for which only single resonances were observed at δ^{31}P = 15.2 ppm (^1J(P,W) = 205.0 Hz) and δ^{29}Si = – 17.1 ppm (^1J(Si,P) = 45.6 Hz) confirming the stoichiometry of the reaction. The structure of **8a** was established unequivocally by a single-crystal X-ray analysis (Figure 4),[16] which shows that the four membered ring is nearly planar with

a torsion angle of 7.46(17)° for P1-C1-C2-Si1 and that the P1–Si1 bond (2.3074(8) Å) is slightly elongated owing to steric congestion.

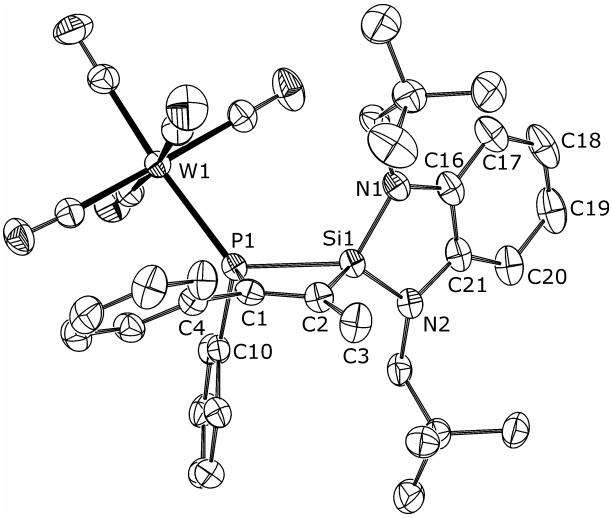


Figure 4. Structure of **8a** in the crystal (displacement ellipsoids drawn at the 50% probability level; hydrogen atoms are omitted for clarity). Selected bond lengths [Å], angles and torsion angles [°]: W1-P1 2.5269(6), P1-Si1 2.3074(8), P1-C1 1.854(2), P1-C10 1.841(2), Si1-N1 1.726(2), Si1-N2 1.7249(19), Si1-C2 1.863(2), C1-C2 1.360(3), C1-C4 1.489(3), C2-C3 1.507(3); C1-P1-Si1 73.30(7), P1-Si1-C2 76.89(7); P1-C1-C2-Si1 7.46(17).

SCS-MP2/6-311+G** calculations on B3LYP/6-31G* model structures containing carbon substituents[22] show that intermediate 2-phospha-4-silabicyclo[1.1.0]butane **4C** can isomerize to the thermodynamically preferred 1,2-dihydro-1,2-phosphasiletes **8A** and **8B** with barriers of only 21.3 and 21.6 kcal·mol^{-1}, respectively. This similarity in $\Delta E^{\ddagger}$ values is reflected in the two experimentally observed isomers. The valence isomerization of **4C** to **8** is symmetry allowed and can be described as a [σ2s+σ2a] process.[26] Such a pathway is unprecedented for the analogous isomerization of bicyclo[1.1.0]butane, for which *s-trans*-1,3-butadiene is the favored product.

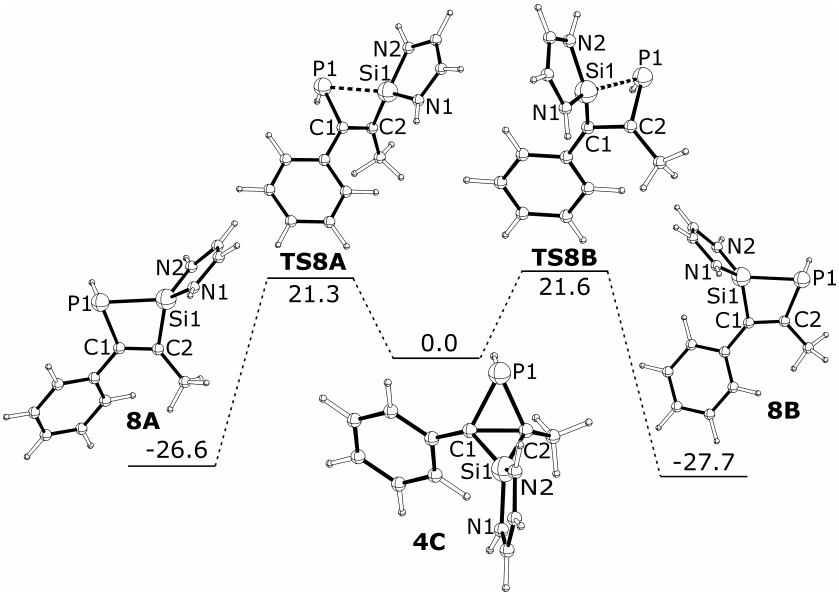


Figure 5. Relative SCS-MP2/6-311+G**//B3YLP/6-31G* energies (in kcal·mol^{-1}) for the direct rearrangement of **4C** into the valence isomers **8A** and **B**. Selected bond lengths [Å], angles and torsion angles [°] of **4C**: P1-C1 1.867, P1-C2 1.875, Si1-C1 1.846, Si1-C2 1.825, C1-C2 1.615, C1-P1-C2 51.1, N1-Si1-N2 91.4, C1-Si1-C2 52.2, P1-C1-C2-Si1 117.1; **TS8A**: P1-Si1 2.498, P1-C1 1.841, P1-C2 2.284, Si1-C1 2.045, Si1-C2 1.780, P1-C1-C2-Si1 80.1; **TS8B**: P1-Si1 2.546, P1-C1 2.389, P1-C2 1.853, Si1-C1 1.789, Si1-C2 1.973, P1-C1-C2-Si1 81.7; **8A**: P1-Si1 2.312, P1-C1 1.888, Si1-C2 1.864, C1-C2 1.368, Si1-P1-C1 71.6, P1-Si1-C2 78.9; **8B**: P1-Si1 2.313, P1-C2 1.878, Si1-C1 1.870, C1-C2 1.367, Si1-P1-C2 71.6, P1-Si1-C1 78.6.

7.5 Conclusion

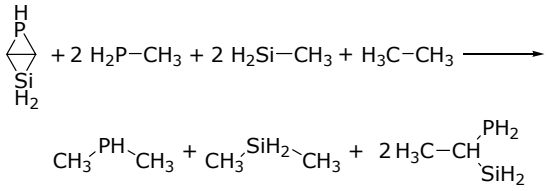
Thermally stable silylene **3** reacts with 1*H*-phosphirenes **2** to give the first isolated 2,3-dihydro-1,3-phosphasiletes **5**, zwitterion **6b** and 1,2-dihydro-1,2-phosphasiletes **8** with the novel 2-phospha-4-silabicyclo[1.1.0]butanes **4** being a reactive intermediate in the reaction, the course of which can be tuned by changing the substituents.

7.6 Computational Section

All electronic structure calculations were performed using the GAUSSIAN 98 suite of programs (G98).[22] Becke's three-parameter hybrid exchange functional combined with the Lee-Yang-Parr correlation functional, denoted as B3LYP, and the 6-31G* basis set was used for the density

functional theory (DFT) calculations.[22] First and second order energy derivatives were computed to confirm that minima or transition structures had been located. Intrinsic reaction coordinate driving calculations (IRC) were performed to establish connections between transition structures and minima. Single point energies calculations at the SCS-MP2/6-311+G** level of theory were performed on B3LYP/6-31G* optimized geometries. SCS-MP2, developed by prof. S. Grimme,[22d] is a simple modification to MP2 theory and gives improved reaction energies.[27]

Ring strain. We calculated a strain energy of 57.9 kcal·mol^{-1} for the parent 2-phospha-4-silabicyclo[1.1.0]butane $PSiC_2H_5$ (C_s symmetry) at the G3(MP2) level of theory[28] using homodesmotic reactions[29] (eqn. 1).



(1)

7.7 Experimental Section

All experiments were performed under an atmosphere of dry argon, by using standard Schlenk techniques. Solvents were purified, dried, and degassed by standard techniques. NMR spectra were recorded (298K) on Bruker Advance 250 (^{31}P; 85% H_3PO_4) and MSL 400 (^{1}H, ^{13}C, ^{29}Si; $SiMe_4$), internally referenced to residual solvent resonances. High-resolution mass spectra (HR-MS) were recorded on a Finnigan Mat 900 and IR spectra on a Mattson-6030 Galaxy spectrophotometer. Melting points were measured on samples in unsealed capillaries and are uncorrected. Compounds **2a**[14] and **3**[13] were prepared according to literature procedures.

2b: [5,6,7-Trimethyl-2,3-bis(methoxycarbonyl)-7-phospha-norbornadiene]pentacarbonyltungsten[30] (217 mg, 0.37 mmol), phenylacetylene (0.40 mL, 3.66 mmol) and CuCl (10 mg, 0.1 mmol) were heated at 60 °C for 6 h in toluene. Evaporation to dryness and chromatography of the residue over silica with pentane/dichloromethane (9/1) as eluent gave 83 mg (48%) of **2b** as a colorless solid: mp 46 °C; ^{31}P{^{1}H} NMR (101.3 MHz, $CDCl_3$): δ = – 161.8 (^1J(P,W) = 267.3 Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 26.2 (d, ^1J(C,P) = 1.9 Hz, ^2J(C,W) = 10.0 Hz; *C*H$_3$), 126.6 (d, ^2J(C,P) = 7.0 Hz; *ipso*-Ph), 129.0 (d, ^1J(C,P) = 37.9 Hz; =*C*-H), 129.2 (d, ^4J(C,P) = 0.8 Hz; *m*-Ph), 129.9 (d, ^3J(C,P) = 4.5 Hz; *o*-Ph), 131.2 (s; *p*-Ph), 142.5 (d, ^1J(C,P) = 12.6 Hz; =*C*-Ph), 196.1 (d, ^1J(C,W) = 125.5 Hz, ^2J(C,P) = 8.7 Hz; *cis*-CO), 198.4 (d, ^2J(C,P) = 30.1 Hz; *trans*-CO); ^{1}H NMR (250.1 MHz, $CDCl_3$): δ = 1.65 (dd, ^2J(H,P) = 5.6 Hz, ^4J(H,H) = 1.0 Hz, 3H; C*H*$_3$), 7.48-7.57 (m, 3H; *m*-Ph-*H*, *p*-Ph-*H*), 7.68-7.75 (m, 2H; *o*-Ph-*H*), 8.31 (dq, ^2J(H,P) = 22.0 Hz, ^4J(H,H) = 1.0 Hz, 1H; C*H*); HR-MS (EI, 70 eV): *m/z* (%): 472 (48) [*M*]$^+$, 388 (52) [*M* – 3CO]$^+$;

calcd for $C_{14}H_9O_5PW$: 471.96973; found: 471.97190; IR (KBr): ν = 1923 (s/br, CO_{eq}), 2072 (w, CO_{ax}).

2c: [5,6-Dimethyl-2,3-bis(methoxycarbonyl)-7-phenyl-7-phosphanorbornadiene]pentacarbonyl-tungsten[30] (0.73 g, 1.12 mmol), 1-phenyl-1-propyne (0.42 mL, 3.36 mmol) and CuCl (10 mg, 0.1 mmol) were heated at 60 °C for 7 h in toluene. Evaporation to dryness and chromatography of the residue over silica with pentane/dichloromethane (9/1) as eluent followed by crystallization from pentane at – 20 °C gave 0.39 g (64%) of **2c** as colorless crystals: mp 118 °C; $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$): δ = – 155.2 (^1J(P,W) = 267.3 Hz); ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 12.3 (d, ^2J(C,P) = 6.7 Hz, *C*H$_3$), 126.8 (d, ^2J(C,P) = 6.9 Hz; *ipso*-Ph), 127.9 (d, ^1J(C,P) = 7.8 Hz; =*C*-Ph), 128.5 (d, ^3J(C,P) = 10.4 Hz; *m*-PhP), 129.2 (s; *m*-Ph), 129.8 (d, ^1J(C,P) = 10.4 Hz; *ipso*-PhP), 130.0 (d, ^3J(C,P) = 5.0 Hz; *o*-Ph), 130.1 (s; *p*-Ph), 130.4 (d, ^4J(C,P) = 2.5 Hz; *p*-PhP), 131.3 (d, ^2J(C,P) = 15.8 Hz; *o*-PhP), 138.2 (d, ^1J(C,P) = 4.8 Hz; =*C*-Me), 196.1 (d, ^1J(C,W) = 125.4 Hz, ^2J(C,P) = 8.6 Hz; *cis*-CO), 198.1 (d, ^2J(C,P) = 30.5 Hz; *trans*-CO); ^1H NMR (400.13 MHz, $CDCl_3$): δ = 2.67 (d, ^3J(H,P) = 9.7 Hz, 3H; C*H*$_3$), 7.34-7.40 (m, 3H; *m*-Ph*H*P, *p*-Ph*H*P), 7.40-7.52 (m, 5H; *m*,*p*-Ph*H*C=, *o*-Ph*H*P), 7.65-7.69 (m, 2H; *o*-Ph*H*C=); HR-MS (EI, 70 eV): *m/z* (%): 548 (44) [*M*]$^+$, 494 (8) [*M* – 2CO]$^+$, 464 (15) [*M* – 3CO]$^+$, 436 (28) [*M* – 4CO]$^+$, 406 (100) [*M* – 5CO]$^+$; calcd for $C_{20}H_{13}O_5PW$: 548.0010; found: 548.0020; IR (KBr): ν = 1910, 1929 (s/br, CO_{eq}), 1991 (w, CO_{eq}), 2070 (w, CO_{ax}).

5a: Complex **2a**[14] (38.6 mg, 72.3 µmol) in *n*-hexane (5 mL) was added slowly to a stirred solution of **3**[13] (39.7 mg, 144.6 µmol) in *n*-hexane (2 mL) at –50 °C. The mixture was warmed to ambient temperature and stirred for 16 h, then filtered. The orange filtrate was concentrated *in vacuo* and cooled at –20 °C affording red crystals of **5a** (56 mg, 66%): mp 245 °C (decomp.); ^{29}Si NMR (79.5 MHz, C_6D_6): δ = – 5.1 (d, ^2J(Si,P) = 6.9 Hz; Ph-*Si*NN), – 13.5 (d, ^2J(Si,P) = 31.8 Hz; *Si*NN); $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$): δ = 278.3 (^1J(P,W) = 254.0 Hz); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 28.3, 28.8, 29.2 and 30.3 (s; C(*C*H$_3$)$_3$), 32.9, 33.2, 33.9 and 34.5 (s; *C*(CH$_3$)$_3$), 34.7 (d, ^1J(C,P) = 18.5 Hz; *C*H), 52.8, 56.5, 56.7 and 58.4 (s; *C*H$_2$), 109.3, 109.6, 109.9, 110.0, 117.2, 117.4, 117.4 and 118.2 (s; N*Ph*H), 126.6 (d, ^3J(C,P) = 18.2 Hz; *o*-Ph), 128.3 (s; *m*-SiPh), 128.5 (d, ^4J(C,P) = 3.1 Hz; *m*-Ph), 128.7 (s; *p*-Ph), 131.1 (s; *p*-SiPh), 135.3 (s; *ipso*-SiPh), 135.6 (s; *o*-SiPh), 138.7 (d, ^2J(C,P) = 2.4 Hz; *ipso*-Ph), 140.5, 140.9, 142.5 and 142.7 (s; N-*ipso*-*Ph*), 194.5 (d, ^2J(C,P) = 8.0 Hz, ^1J(C,W) = 126.8 Hz; *cis*-CO), 197.3 (d, ^1J(C,P) = 3.5 Hz; P=*C*), 197.4 (d, ^2J(C,P) = 30.5 Hz; *trans*-CO); ^1H NMR (400.1 MHz, $CDCl_3$): δ = 0.36, 0.48, 1.07 and 1.10 (s, 9H; C(C*H*$_3$)$_3$), 2.20, 2.26, 2.28, 2.32 (AB type, ^2J(H,H) = 14.9 Hz, 2H; C*H*$_2$), 2.28, 2.32, 2.41, 2.45 (AB type, ^2J(H,H) = 15.1 Hz, 2H; C*H*$_2$), 3.13, 3.17, 3.32, 3.36 (AB type, ^2J(H,H) = 14.7 Hz, 2H; C*H*$_2$), 3.27, 3.31, 3.42, 3.45 (AB type, ^2J(H,H) = 14.7 Hz, 2H; C*H*$_2$), 3.58 (d, ^2J(H,P) = 18.9 Hz, 1H; C*H*), 6.44-6.51 (m, 2H; NPh*H*), 6.65-6.71 (m, 4H; NPh*H*), 6.79-6.82 (m, 2H; NPh*H*), 7.25-7.34 (m, 3H; *m*-Ph*H*, *p*-Ph*H*), 7.42-7.48 (m, 5H; *o*-Ph*H*, *m*-SiPh*H*, *p*-SiPh*H*), 7.72-7.74 (m, 2H; *o*-SiPh*H*); HR-MS (EI, 70 eV): *m/z* (%): 1082 (2) [*M*]$^+$, 998

(60) [*M* – 3CO]$^+$, 941 (15) [*M* – 3CO – *t*Bu]$^+$, 758 (100) [*M* – W(CO)$_5$]$^+$, 701 (70) [*M* – W(CO)$_5$ – *t*Bu]$^+$; calcd for $C_{51}H_{63}O_5N_4Si_2PW$: 1082.35840; Found: 1082.35376; IR (KBr): ν = 1944, 1960 (s/br, CO_{eq}), 2077 (m, CO_{ax}).

5b: Complex **2b** (12.3 mg, 26.0 µmol) and **3**[13] (14.3 mg, 52.1 µmol) were heated at 75 °C for 2 h in C_6D_6 (0.5 mL). Evaporation to dryness and extraction into *n*-hexane gave after filtration and cooling at –20 °C red crystals of **5b** (15 mg, 57%): mp 150 °C (decomp.); ^{29}Si NMR (79.5 MHz, C_6D_6): δ = 4.8 (d, ^2J(Si,P) = 4.2 Hz; Me-*Si*NN), – 13.8 (d, ^2J(Si,P) = 33.2 Hz; *Si*NN); ^{31}P{^{1}H} NMR (101.3 MHz, C_6D_6): δ = 276.6 (^1J(P,W) = 246.1 Hz); ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δ = 5.2 (s; *C*H$_3$), 28.7, 29.2, 29.3 and 30.0 (s; C(*C*H$_3$)$_3$), 33.3, 33.4, 33.9 and 34.6 (s; *C*(CH$_3$)$_3$), 41.1 (d, ^1J(C,P) = 18.4 Hz; *C*H), 52.7, 56.7, 57.0 and 57.5 (s; *C*H$_2$), 110.1, 110.2, 110.4, 110.6, 118.0, 118.1, 118.1 and 118.6 (s; N*Ph*H), 126.8 (d, ^3J(C,P) = 18.4 Hz; *o*-Ph), 128.9 (d, ^4J(C,P) = 2.8 Hz; *m*-Ph), 129.0 (s; *p*-Ph), 139.0 (d, ^2J(C,P) = 2.0 Hz; *ipso*-Ph), 140.9, 141.0, 142.3 and 142.9 (s; N-*ipso*-*Ph*), 195.1 (d, ^2J(C,P) = 8.0 Hz; *cis*-CO), 197.4 (d, ^1J(C,P) = 4.0 Hz; P=*C*), 197.6 (d, ^2J(C,P) = 29.9 Hz; *trans*-CO); ^{1}H NMR (400.1 MHz, C_6D_6): δ = 0.64 and 0.67 (s, 9H; C(C*H*$_3$)$_3$), 0.87 (s, 3H; C*H*$_3$), 1.02 and 1.09 (s, 9H; C(C*H*$_3$)$_3$), 2.34, 2.37, 2.47, 2.51 (AB type, ^2J(H,H) = 15.1 Hz, 2H; C*H*$_2$), 2.53 (s, 2H; C*H*$_2$), 2.90 (d, ^2J(H,P) = 20.3 Hz, 1H; C*H*), 3.10, 3.13, 3.32, 3.36 (AB type, ^2J(H,H) = 14.6 Hz, 2H; C*H*$_2$), 3.31, 3.35, 3.37, 3.41 (AB type, ^2J(H,H) = 14.6 Hz, 2H; C*H*$_2$), 6.57-6.63 (m, 2H; NPh*H*), 6.76-6.86 (m, 6H; NPh*H*), 6.93-6.98 (m, 1H; *p*-Ph*H*), 7.08-7.13 (m, ^3J(H,H) = 7.8 Hz, 2H; *m*-Ph*H*), 7.58-7.61 (m, ^3J(H,H) = 7.8 Hz, 2H; *o*-Ph*H*); HR-MS (EI, 70 eV): *m/z* (%): 1020 (5) [*M*]$^+$, 936 (6) [*M* – 3CO]$^+$, 766 (2) [*M* – 5CO – 2*t*Bu]$^+$, 696 (5) [*M* – W(CO)$_5$]$^+$; calcd for $C_{46}H_{61}O_5N_4Si_2PW$: 1020.34277; Found: 1020.3391; IR (KBr): ν = 1941 (s/br, CO_{eq}), 2074 (m, CO_{ax}).

6b: Complex **2b** (20.4 mg, 43.2 µmol) in *n*-hexane (5 mL) was added to a stirred solution of **3**[13] (23.7 mg, 86.3 µmol) in *n*-hexane (2 mL) at ambient temperature and stirred for 2 h. The solution was concentrated *in vacuo* and cooled at 0 °C affording yellow crystals of **6b** (30 mg, 68%): mp 149 °C (decomp.); ^{29}Si NMR (79.5 MHz, C_6D_6): δ – 33.4 (d, ^2J(Si,P) = 18.4 Hz; PhC-*Si*NN), – 11.2 (d, ^2J(Si,P) = 17.2 Hz; *Si*NN); ^{31}P{^{1}H} NMR (101.3 MHz, C_6D_6): δ = – 6.8 (^1J(P,W) = 240.0 Hz); ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δ = 28.9, 29.0, 29.2 and 30.5 (s; C(*C*H$_3$)$_3$), 32.9, 34.5, 34.6 and 34.9 (s; *C*(CH$_3$)$_3$), 34.7 (d, ^1J(C,P) = 11.4 Hz; *C*H), 36.6 (d, ^1J(C,P) = 4.4 Hz; *C*H$_3$), 51.8, 53.0 and 56.2 (s; *C*H$_2$), 59.5 (d, ^1J(C,P) = 24.9 Hz; *C*-Ph), 60.2 (s; *C*H$_2$), 112.4, 112.7, 112.8, 117.9 and 118.9 (s; N*Ph*H), 119.7 (s; *p*-Ph), 119.9 (s; N*Ph*H), 123.6 (s; N*Ph*H), 125.3 (d, ^3J(C,P) = 14.3 Hz; *o*-Ph), 127.6 (s; N*Ph*H), 128.5 (d, ^4J(C,P) = 2.4 Hz; *m*-Ph), 130.5, 136.5 and 138.2 (s; N-*ipso*-*Ph*), 142.8 (d, ^2J(C,P) = 5.9 Hz; *ipso*-Ph), 145.5 (s; N-*ipso*-*Ph*), 199.3 (d, ^1J(C,W) = 126.1 Hz, ^2J(C,P) = 7.3 Hz; *cis*-CO), 200.8 (d, ^2J(C,P) = 20.5 Hz; *trans*-CO); ^{1}H NMR (400.1 MHz, C_6D_6): δ = 0.52, 0.82, 0.93 and 1.04 (s, 9H; C(C*H*$_3$)$_3$), 2.31, 2.34, 2.66, 2.70 (AB type, ^2J(H,H) = 14.5 Hz, 2H; C*H*$_2$), 2.57 (d, ^2J(H,P) = 5.0 Hz, 3H; C*H*$_3$), 2.91, 2.95, 3.27, 3.31 (AB type, ^2J(H,H) = 13.5 Hz, 2H; C*H*$_2$), 3.03, 3.07, 3.49, 3.53 (AB type, ^2J(H,H)

= 14.4 Hz, 2H; CH_2), 3.27, 3.30, 3.52, 3.56 (AB type, ^2J(H,H) = 13.45 Hz, 2H; CH_2), 3.78 (d, ^2J(H,P) = 8.4 Hz, 1H; C*H*), 5.79 (dd, ^3J(H,H) = 7.9 Hz, ^4J(H,H) = 1.3 Hz, 1H; NPh*H*), 6.28 (dt, ^3J(H,H) = 7.8 Hz, ^4J(H,H) = 1.1 Hz, 1H; NPh*H*), 6.36-6.40 (m, 1H, NPh*H*), 6.61 (dd, ^3J(H,H) = 8.3 Hz, ^4J(H,H) = 1.0 Hz, 1H; NPh*H*), 7.76-7.85 (m, 4H; NPh*H*), 6.89-6.93 (m, 1H; *p*-Ph*H*), 7.18-7.21 (m, 2H; *o*-Ph*H*), 7.31-7.36 (m, 2H; *m*-Ph*H*);

8: Complex **2c** (44.9 mg, 81.9 µmol) and **3**[13] (33.7 mg, 122.8 µmol) were heated at 80 °C for 13 h in C_6D_6 (0.5 mL). NMR-yields: $^{31}P\{^1H\}$ NMR (101.3 MHz, C_6D_6): δ = 12.0 (^1J(P,W) = 198.5 Hz, 19% of **8b**), 15.2 (^1J(P,W) = 205.6 Hz, 50% of **8a**), 308.1 (br. s, 19.5% of **5c**). Evaporation to dryness and extraction into *n*-hexane gave after cooling at – 80 °C yellow crystals of **8a** (30 mg, 45%). **8a**: mp 157 °C (decomp.); ^{29}Si NMR (79.5 MHz, C_6D_6): δ – 17.1 (d, ^1J(Si,P) = 45.6 Hz; *Si*NN); $^{31}P\{^1H\}$ NMR (101.3 MHz, C_6D_6): δ = 15.2 (^1J(P,W) = 205.0 Hz); $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6): δ = 19.3 (d, ^3J(C,P) = 16.8 Hz; *C*H_3), 28.7 and 29.1 (s; C(*C*H_3)$_3$), 33.6 and 34.5 (s; *C*(CH$_3$)$_3$), 53.4 and 55.3 (s; *C*H_2), 110.3, 111.0, 118.8 and 119.2 (s; N*Ph*H), 128.9 (d, ^4J(C,P) = 2.3 Hz; *p*-PhP), 129.0 (d, ^3J(C,P) = 8.8 Hz; *m*-PhP), 129.1 (s; *m*-Ph), 129.4 (s; *p*-Ph), 129.5 (d, ^3J(C,P) = 2.8 Hz; *o*-Ph), 130.8 (d, ^2J(C,P) = 11.3 Hz; *o*-PhP), 136.7 (d, ^2J(C,P) = 11.8 Hz; *ipso*-Ph), 138.2 (d, ^1J(C,P) = 11.0 Hz; *ipso*-PhP), 139.0 and 139.4 (s; N-*ipso*-*Ph*), 155.3 (d, ^2J(C,P) = 61.7 Hz; =*C*-Me), 165.7 (d, ^1J(C,P) = 25.3 Hz; =*C*-Ph), 197.5 (d, ^1J(C,W) = 125.7, ^2J(C,P) = 5.5 Hz; *cis*-CO), 199.4 (d, ^2J(C,P) = 21.1 Hz; *trans*-CO); ^{1}H NMR (400.1 MHz, C_6D_6): δ = 0.69 and 1.01 (s, 9H; C(CH_3)$_3$), 1.73, 1.77, 2.72, 2.75 (AB type, ^2J(H,H) = 14.9 Hz, 2H; CH_2), 1.99 (s, 3H; CH_3), 3.55, 3.58, 3.77, 3.80 (AB type, ^2J(H,H) = 14.8 Hz, 2H; CH_2), 6.73-6.77 (m, 1H; *p*-Ph*H*P), 6.82-6.97 (m, 6H; NPh*H*, *m*-Ph*H*P), 7.08-7.13 (m, 1H; *p*-Ph*H*), 7.18-7.22 (m, 2H; *o*-Ph*H*), 7.28-7.34 (m, 2H; *o*-Ph*H*P), 7.51-7.54 (m, 2H; *o*-Ph*H*); HR-MS (EI, 70 eV): *m/z* (%): 822 (80) [*M*]$^+$, 766 (58) [*M* – 2CO]$^+$, 738 (43) [*M* – 3CO]$^+$, 682 (24) [*M* – 5CO]$^+$, 625 (10) [*M* – 5CO – *t*Bu]$^+$, 498 (100) [*M* – W(CO)$_5$]$^+$, 441 (22) [*M* – W(CO)$_5$ – *t*Bu]$^+$; calcd for $C_{36}H_{39}O_5N_2SiPW$: 822.1876; Found: 822.1880; IR (KBr): ν = 1929 (s/br, CO_{eq}), 1979 (w, CO_{eq}), 2068 (m, CO_{ax}). **8b**: $^{31}P\{^1H\}$ NMR (101.3 MHz, C_6D_6): δ = 12.2 (^1J(P,W) = 199.5 Hz).

5c: MS (EI, 70 eV): *m/z* (%): 1096 (30) [*M*]$^+$, 1012 (22) [*M* – 3CO]$^+$, 956 (2) [*M* – 5CO]$^+$, 899 (3) [*M* – 5CO – *t*Bu]$^+$, 772 (42) [*M* – W(CO)$_5$]$^+$.

7.8 References and Notes

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[16] Crystal structure determinations: X-ray intensities were measured on a Nonius KappaCCD diffractometer with rotating anode (λ=0.71073 Å) at a temperature of 150(2) K. The structures were refined with SHELXL97[31] against F2 of all reflections. Illustrations, structure calculations and checking was performed with the PLATON package.[32] Compound **5a** ($C_{51}H_{63}N_4O_5PSi_2W{\cdot}0.6(C_6H_{14})$): M_w = 1134.76, red block, 0.06 x 0.18 x 0.21 mm^3, monoclinic, *P*21 (No. 4), *a* = 10.5532(1), *b* = 16.0049(2), *c* = 17.2900(2) Å, β = 100.5233(5), *V* = 2871.21(6) Å3, *Z* = 2, ρ = 1.313 g cm-3. 51129 measured reflections, 13052 unique reflections (*R*int = 0.050); structure solution with automated Patterson methods;[33] 643 refined parameters, 46 restraints; *R*1/*wR*2 [$I > 2\sigma(I)$]: 0.0338/0.0755, *R*1/*wR*2 (all reflections) = 0.0472/0.0794; GoF = 1.072; Flack x parameter: -0.024(4). **6b** ($C_{46}H_{61}N_4O_5PSi_2W$): M_w = 1020.99, yellow block, 0.18 x 0.24 x 0.30 mm3, triclinic, $P\overline{1}$

(No. 2), *a* = 10.6476(3), *b* = 21.2390(8), *c* = 22.6862(5) Å, α = 74.495(2), β = 89.5698(19), γ = 82.814(3)°, *V* = 4903.0(3) Å3, *Z* = 4, ρ = 1.383 g cm-3. The crystal appeared to be non-merohedrally twinned with a 180° rotation about *uvw* = [100] as twin operation. The intensity data were evaluated with EvalCCD,[34] taking this twin relation into account; 55937 measured reflections, 22336 unique reflections (*R*int = 0.058); structure solution with direct methods;[35] 1064 refined parameters, 388 restraints; bond lengths and angles of the two independent molecules were restrained to be the same; *R*1/*wR*2 [$I > 2\sigma(I)$]: 0.0499/0.1070, *R*1/*wR*2 (all reflections) = 0.0767/0.1216; GoF = 1.128; the refinement[31] of the twin fraction resulted in 0.794(1):0.206. **8a** ($C_{36}H_{39}N_2O_5PSiW$): M_w = 822.60, yellow plate, 0.06 x 0.36 x 0.42 mm3, monoclinic, *P*21/c (No. 14), *a* = 19.1665(1), *b* = 10.6482(1), *c* = 20.5181(1) Å, β = 119.8343(4)°, *V* = 3632.53(5) Å3, *Z* = 4, ρ = 1.504 g cm-3; 58693 measured reflections, 8329 unique reflections (*R*int = 0.046); structure solution with automated Patterson methods;[33] 422 refined parameters, no restraints; *R*1/*wR*2 [$I > 2\sigma(I)$]: 0.0204/0.0455, *R*1/*wR*2 (all reflections) = 0.0289/0.0488; GoF = 1.038. CCDC-216769 (**5a**), -216770 (**6b**) and -232111 (**8a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336033; or: deposit@ccdc.cam.ac.uk).

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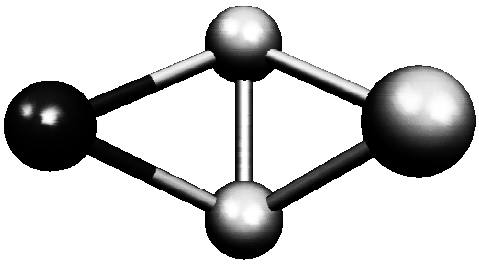
Valence Isomerization of 2-Phospha-4-silabicyclo[1.1.0]butane

A High-level Ab Initio Study

8

The rearrangements for 2-phospha-4-silabicyclo[1.1.0]butane (see picture), analogous to the valence isomerization of the hydrocarbons bicyclobutane, 1,3-butadiene and cyclobutene, were studied at the (U)QCISDT/6–311+G**//(U)QCISD/6–31G* level of theory. The monocyclic 1,2-dihydro-1,2-phosphasiletes are shown to be the thermodynamically preferred product, in contrast to the isomerization of the hydrocarbons that favors the 1,3-butadiene structure. Furthermore, an unprecedented direct isomerization pathway to the 1,2-dihydro-1,2-phosphasiletes was identified, which is competitive with the isomerization via the open-chain butadienes and becomes favorable when electron donating substituents are present on silicon.



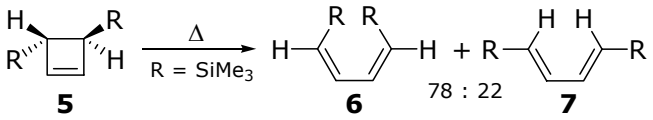
Published in: a) *Phosphorus, Sulfur, and Silicon* **2004**, *179*, 803–807;
b) *J. Mol. Model*. **2005**, *11*, in press.

8.1 Introduction

Bicyclo[1.1.0]butane, with its strain energy of over 60 kcal·mol^{-1}, is a fascinating compound that has attracted the interest of both experimental and theoretical chemists.[1] It is now well established that bicyclo[1.1.0]butane (**1**) opens to the more stable valence isomer *gauche*-butadiene (**2**) by a pericyclic rearrangement, which is characterized by a concerted, asynchronous conrotatory ring opening, where the central C–C bond remains intact.[2,3] This is an allowed [σ2s+σ2a] conrotatory rearrangement according to the Woodward–Hoffmann (W–H) orbital symmetry rules[4] affording kinetic **2** that can easily rotate to *s-trans*-1,3-butadiene **3**. The activation barrier of 41.5 kcal·mol^{-1} calculated at the multiconfiguration self-consistent field level of theory[2] agrees closely with the experimental value of 40.6 kcal·mol^{-1}.[5] The disrotatory, W–H forbidden, thermal ring opening of **1** is less favorable and was calculated to be about 15 kcal·mol^{-1} higher in energy.[2] Another rearrangement is also feasible, stretching of the central C–C bond leads to a planar singlet diradical transition structure for inversion, which is also a higher energy process with a barrier of 47.4 kcal·mol^{-1}.[6]

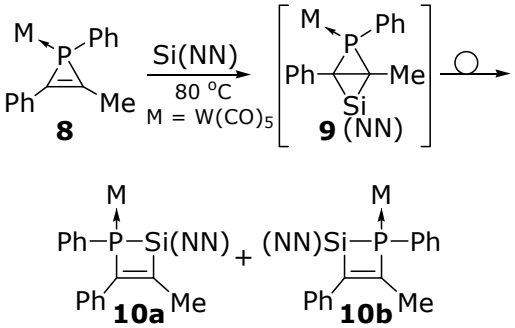
1 **2** **3** **4**

Valence isomer cyclobutene (**4**) is of intermediate stability between **1** and **3** and converts thermally to *gauche*-butadiene **2** by an electrocyclic ring opening.[7] This pericyclic rearrangement follows a W–H allowed concerted, conrotatory pathway. The calculated activation barrier at the MP2/6–311G** level of theory of 33.7 kcal·mol^{-1}[8] for this process is in agreement with the experimental value of 32.9 ± 0.5 kcal·mol^{-1}.[7] Usually for the ring opening of cyclobutenes, steric effects dominate the preference for inward vs. outward rotation,[9] however, electronic effects can also dictate this rearrangement as was reported recently for the sterically hindered substrate **5** that prefers to react via the more crowded inward rotatory pathway leading mainly to butadiene **6** (Scheme 1).[10]



Scheme 1. Ring opening of cyclobutene **5**.

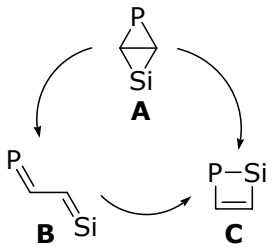
Bicyclo[1.1.0]butanes with main group hetero elements in the ring have also received considerable attention.[11] However, little is known about the phosphorus containing analogues.[12] In our ongoing research on small strained organophosphorus ring systems we became interested in the yet unknown 2-phospha-4-silabicyclo[1.1.0]butanes, of which we recently have reported its occurrence as a reactive intermediate.[13] Valence isomerization of the complexed 2-phospha-4-silabicyclo[1.1.0]butane **9** to the 1,2-dihydro-1,2-phosphasiletes **10a**,**b** was indicated by reacting 1*H*-phosphirene **8** with silylene Si[(NCH$_2$^{t}Bu)$_2$C$_6$H$_4$-1,2] [≡Si(NN)] (Scheme 2).



Scheme 2. Isomerization of bicyclo[1.1.0]butane **9**.

SCS-MP2/6–311+G** calculations on B3LYP/6–31G* model structures show that the intermediate 2-phospha-4-silabicyclo[1.1.0]butane isomerizes directly, via an unprecedented W–H allowed [σ2s+σ2a] process, to the thermodynamically preferred 1,2-dihydro-1,2-phosphasilete.[13] This pathway is favored over the concerted, asynchronous conrotatory ring opening leading to *s-trans*-1-phospha-4-sila-1,3-butadiene.[14]

Here we report on the isomerization of 2-phospha-4-silabicyclo[1.1.0]butane **A** to its valence isomers 1-phospha-4-sila-1,3-butadiene **B** and 1,2-dihydro-1,2-phosphasilete **C**[15] using high-level ab initio calculations at the (U)QCISDT/6–311+G**//(U)QCISD/6–31G* level of theory. We will compare the differences between a direct **A**→**C** pathway versus the isomerization via butadiene **B**. In addition, also the influence of substituents on silicon on the rearrangements will be discussed.



First, we investigated the rearrangements of bicyclo[1.1.0]butane (**1**) and cyclobutene (**4**) into the more stable *s*-trans-1,3-butadiene (**3**) at the (U)QCISDT/6–311+G**//(U)QCISD/6–31G* level of theory,[16] since no complete study of the valence isomerizations of all C_4H_6 isomers at the same level of theory was reported to date. Subsequently, we investigated the rearrangements of the 2-phospha-4-silabicyclo[1.1.0]butanes where the effects of heteroatom substitution will become apparent on the characteristics of the rearrangements.

8.2 Bicyclo[1.1.0]butane

Bicyclo[1.1.0]butane (**1**) leads to *gauche*-butadiene **2** via a concerted, asynchronous conrotatory ring opening[2,3] with a barrier of 39.2 kcal·mol^{-1} and is exothermic by 26.0 kcal·mol^{-1} (Figure 1). This closed-shell rearrangement is favored over the corresponding diradical open-shell pathway ($\Delta E^{\ddagger}$ = 43.2 kcal·mol^{-1}, $<S^2>$ = 0.85). In addition, cyclobutene (**4**) also gives **2**, via a synchronous (C_s symmetry) conrotatory ring opening[8] that requires 32.8 kcal·mol^{-1} and is exothermic by 9.9 kcal·mol^{-1}. Both calculated reaction barriers are in excellent agreement with the experimental values of, respectively, 40.6[5] and 32.9[7] kcal·mol^{-1}.

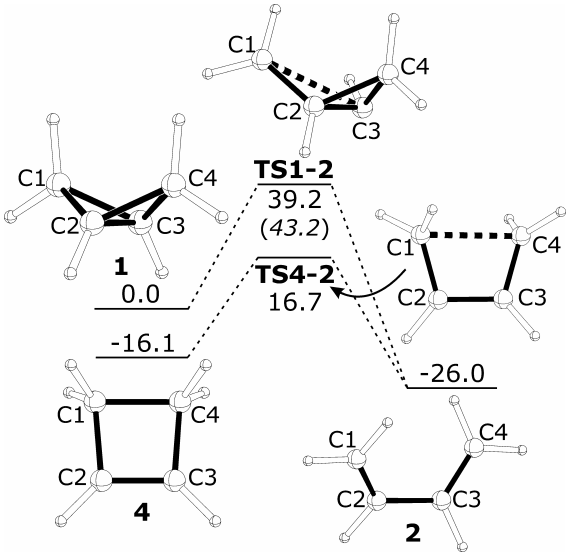


Figure 1. Relative QCISDT/6–311+G**//QCISD/6–31G* (UQCISDT/6–311+G**//UQCISD/6–31G* in parenthesis) energies (ZPE corrected, in kcal·mol^{-1}) for the rearrangements of **1** and **4** into **2**. Selected bond lengths [Å], angles and torsion angles [°] of **1** (C_{2v}): C1-C2 1.498, C2-C3 1.494, C2-C1-C3 59.8, C1-C2-C3-C4 121.9; **2** (C_2): C1-C2 1.342, C2-C3 1.479, C3-C4 1.342, C1-C2-C3-C4 37.9; **4** (C_{2v}): C1-C2 1.520, C1-C4 1.570, C2-C3 1.346, C1-C2-C3 94.2; **TS1-2** (closed-shell): C1-C2 1.403, C1-C3 2.344, C2-C3 1.542, C2-C4 1.569, C2-C1-C3 39.4; **TS4-2** (C_2): C1-C2 1.430, C1-C4 2.150, C2-C3 1.379, C1-C2-C3-C4 21.7.

The kinetic *gauche*-butadiene **2** can easily transform into its enantiomer **2'** via the planar *s-cis*-1,3-butadiene (**TS2-2'**)[2,17] with a barrier of only 0.7 kcal·mol^{-1} or can rotate to the more stable *trans*-butadiene **3** ($\Delta E^{\ddagger}$ = 2.5 kcal·mol^{-1}) with an exothermicity of 2.6 kcal·mol^{-1} (Figure 2).[8] The geometrical parameters of the optimized structures **1**, **3** and **4** at the QCISD/6–31G* level of theory are in excellent agreement with the experimental estimates.[18]

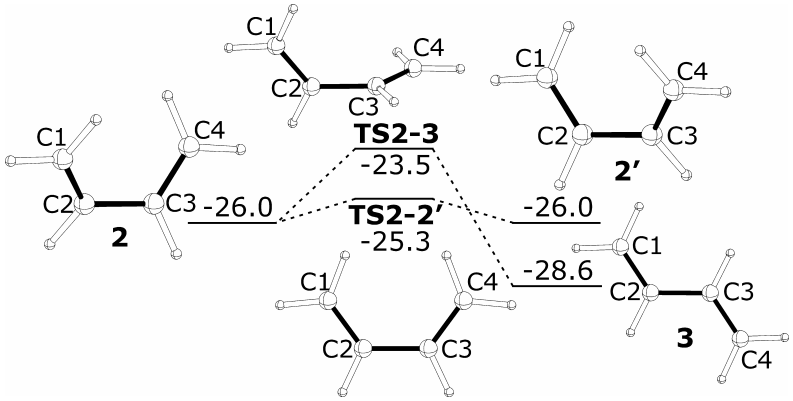


Figure 2. Relative QCISDT/6–311+G**//QCISD/6–31G* energies (ZPE corrected, in kcal·mol^{-1}) for the rearrangements of **2**. Selected bond lengths [Å], angles and torsion angles [°] of **3** (C_{2h}): C1-C2 1.343, C2-C3 1.467, C1-C2-C3 123.8; **TS2-3** (C_2): C1-C2 1.340, C2-C3 1.490, C1-C2-C3-C4 101.9; **TS2-2'** (C_{2v}): C1-C2 1.430, C2-C3 1.379, C1-C2-C3-C4 0.0.

8.3 2-Phospha-4-silabicyclo[1.1.0]butane

Incorporating heteroatoms into the bicyclo[1.1.0]butane framework has a profound impact. We found that 2-phospha-4-silabicyclo[1.1.0]butane (**11**) opens with a modest exothermicity (0.4 kcal·mol^{-1}) directly to valence isomer *s*-1-phospha-4-sila-1,3-butadiene (**12**) in its *trans* configuration via a concerted, asynchronous conrotatory ring opening. In this process the P–C2 bond becomes elongated well before that of the Si–C1 bond (Figure 3). The activation barrier of 38.8 kcal·mol^{-1} is very similar to the calculated activation barrier of 39.2 kcal·mol^{-1} for the [σ2s+σ2a] process in bicyclo[1.1.0]butane (**1**). The closed-shell rearrangement **11**→**12** is favored over the corresponding diradical open-shell pathway ($\Delta E^{\ddagger}$ = 41.3 kcal·mol^{-1}, $<S^2>$ = 0.97).

s-Trans-butadiene **12** can transform into the slightly less stable *gauche*-butadiene **13** (ΔE = 2.6 kcal·mol^{-1}) with an energy barrier of 7.5 kcal·mol^{-1}. Subsequently, butadiene **13** can isomerize via a conrotatory electrocyclic ring closure to the much more stable 1,2-dihydro-1,2-phosphasilete (**14**) (ΔE = –23.9 kcal·mol^{-1}) with a rearrangement barrier of only 3.2 kcal·mol^{-1}. Clearly, if a 1-phospha-4-sila-butadiene is to be formed from **11** it will rearrange to the four-membered ring structure **14**. We conclude that much in contrast to the hydrocarbons, where butadiene **3** is the

favored product, the P,Si-derivatives **12** and **13** are not likely candidates to be observed on rearranging bicyclic compound **11**.

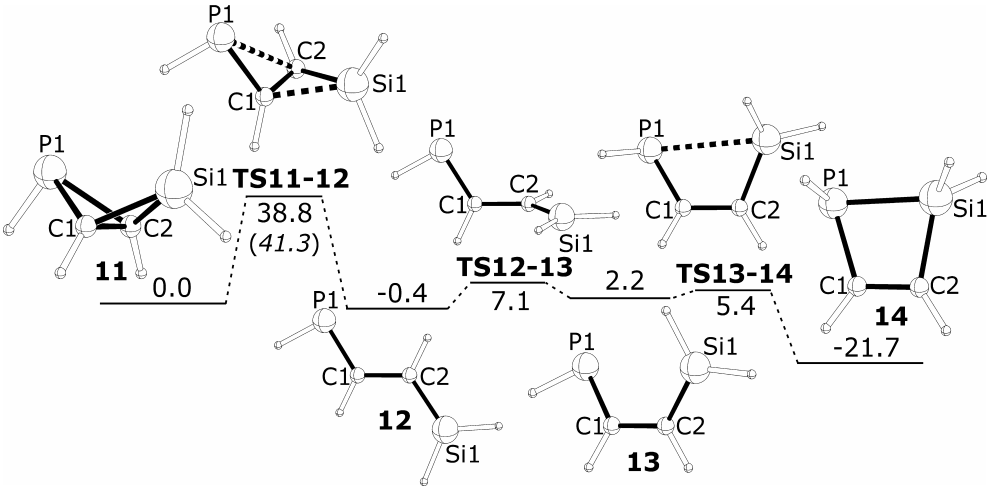


Figure 3. Relative QCISDT/6–311+G**//QCISD/6–31G* (UQCISDT/6–311+G**//UQCISD/6–31G* in parenthesis) energies (ZPE corrected, in kcal·mol^{-1}) for the rearrangements of **11** into **14**. Selected bond lengths [Å], angles and torsion angles [°] of **11** (C_s): P1-C1 1.852, Si1-C1 1.840, C1-C2 1.548, C1-P1-C2 49.4, C1-Si1-C2 49.7, P1-C1-C2-Si1 119.0; **TS11-12**: P1-C1 1.782, P1-C2 2.664, Si1-C1 1.982, Si1-C2 1.785; **12** (C_s): P1-C1 1.708, Si1-C2 1.741, C1-C2 1.443; **TS12-13**: P1-C1-C2-Si1 103.3; **13**: P1-C1-C2-Si1 36.3; **TS13-14**: P1-C1 1.736, P1-Si1 3.001, Si1-C2 1.774, C1-C2 1.414, P1-C1-C2-Si1 34.1; **14**: P1-C1 1.869, P1-Si1 2.290, Si1-C2 1.872, C1-C2 1.354.

As **14** is the thermodynamically preferred valence isomer we also explored whether it could be formed directly from bicyclic **11**. Indeed, forcing an asynchronous conrotatory ring opening with an initial SiH_2 group rotation resulted in transition structure **TS11-14** for the direct rearrangement of **11** into **14** (Figure 4). The barrier of 39.0 kcal·mol^{-1} for this closed-shell process is similar to the conversion via the P,Si-butadienes ($\Delta E^{\ddagger}$ = 38.8 kcal·mol^{-1}, Figure 3).[19] The rearrangement via **TS11-14** obeys the orbital symmetry rules and can be described as a [σ2s+σ2a] process. Such a pathway is unprecedented for the isomerization of the carbon analogue bicyclo[1.1.0]butane (**1**),[2] for which *s-trans*-1,3-butadiene is the favored product.

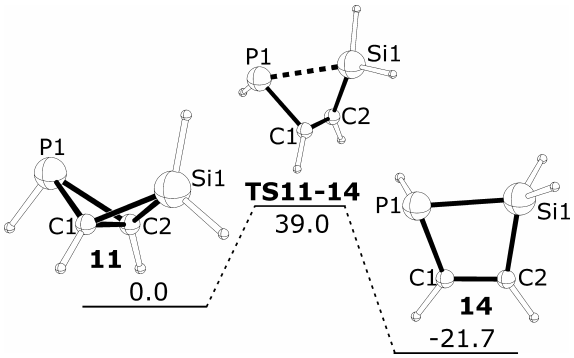


Figure 4. Relative QCISDT/6–311+G**//QCISD/6–31G* energies (ZPE corrected, in kcal·mol^{-1}) for the direct rearrangement of **11** into **14**. Selected bond lengths [Å] and torsion angles [°] of **TS11-14**: P1-C1 1.834, P1-Si1 2.431, Si1-C2 1.800, C1-C2 1.422, P1-C1-C2-Si1 76.0.

8.4 Substituent Effect

Due to the similarities in activation energy for the conversions **11**→**12** and **11**→**14** at the QCISDT/6–311+G**//QCISD/6–31G* level of theory we have also incorporated in our computational model the cyclic diamine HN-C=C-NH as substituent on silicon to investigate the effect of donating N atoms, that are also present in our experimental system,[13] on the rearrangements.

Substituted 2-phospha-4-silabicyclo[1.1.0]butane **15** leads to its valence isomer *s-trans*-1-phospha-4-sila-1,3-butadiene **16** via a concerted, asynchronous conrotatory ring opening ($\Delta E^{\ddagger}$ = 39.0 kcal·mol^{-1}) with a modest endothermicity of 1.5 kcal·mol^{-1} (Figure 5). The associated transition structure **TS15-16** shows features similar to the parent analogue **TS11-12** and the closed-shell rearrangement **15**→**16** is favored over the corresponding diradical open-shell pathway ($\Delta E^{\ddagger}$ = 46.1 kcal·mol^{-1}, $<S^2>$ = 0.97).[20] In addition, *s-trans*-butadiene **16** can transform into the slightly more stable planar *cis*-butadiene **17** (ΔE = –1.5 kcal·mol^{-1}), which is now an energy minimum, with an energy barrier of only 8.2 kcal·mol^{-1}.

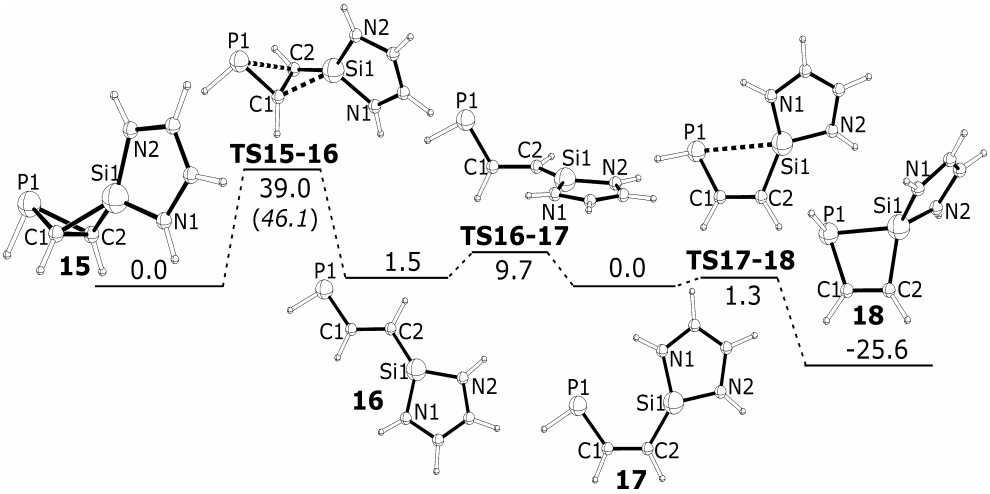


Figure 5. Relative QCISDT/6–311+G**//QCISD/6–31G* (UQCISDT/6–311+G**//UMP2/6–31G* in parenthesis)[20] energies (ZPE corrected, in kcal·mol^{-1}) for the rearrangements of **15** into **18**. Selected bond lengths [Å], angles and torsion angles [°] of **15** (C_s): P1-C1 1.852, Si1-C1 1.823, Si1-N1 1.730, C1-C2 1.613, C1-P1-C2 51.6, C1-Si1-C2 52.5, P1-C1-C2-Si1 122.1; **TS15-16**: P1-C1 1.768, P1-C2 2.590, Si1-C1 1.977, Si1-C2 1.748, Si1-N1 1.726; **16** (C_s): P1-C1 1.718, Si1-C2 1.724, Si1-N1 1.717, C1-C2 1.434; **TS16-17**: P1-C1-C2-Si1 98.2; **17** (C_s): P1-C1 1.727, Si1-C2 1.732, Si1-N1 1.710, Si1-N2 1.717; **TS17-18**: P1-C1 1.743, P1-Si1 3.103, Si1-C2 1.765, Si1-N1 1.719, C1-C2 1.406, P1-C1-C2-Si1 24.8; **18**: P1-C1 1.867, P1-Si1 2.309, Si1-C2 1.867, Si1-N1 1.741, C1-C2 1.356.

Subsequently, **17** can isomerize via a conrotatory electrocyclic ring closure to the much more stable 1,2-dihydro-1,2-phosphasilete **18** (ΔE = –25.6 kcal·mol^{-1}) with a minute barrier of only 1.3 kcal·mol^{-1}. The geometrical parameters of the optimized **18** are in good agreement with the single-crystal X-ray analysis of **10a**.[13]

Interestingly, the direct valence isomerization becomes now favorable and 2-phospha-4-silabicyclo[1.1.0]butane **15** gives cyclobutene derivative **18** ($\Delta E^{\ddagger}$ = 27.7 kcal·mol^{-1}) via a W–H allowed [σ2s+σ2a] process with an exothermicity of 25.6 kcal·mol^{-1} (Figure 6).

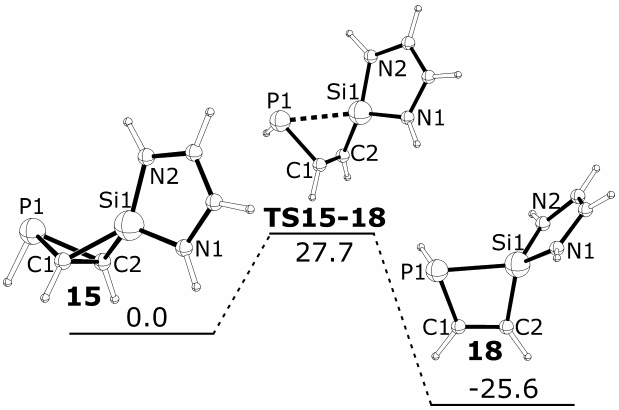


Figure 6. Relative QCISDT/6–311+G**//QCISD/6–31G* energies (ZPE corrected, in kcal·mol^{-1}) for the direct rearrangement of **15** into **18**. Selected bond lengths [Å] and torsion angles [°] of **TS15-18**: P1-C1 1.841, P1-Si1 2.458, Si1-C2 1.777, Si1-N1 1.742, Si1-N2 1.736, C1-C2 1.444, P1-C1-C2-Si1 78.0.

The lower barrier for the direct conversion **15**→**18** compared to that of the parent **11**→**14** can be ascribed to the presence of the donating amino groups on silicon. Generally, *π*-donor (*e.g.* NH_2) and *σ*-acceptor (*e.g.* F) substituents destabilize three-membered rings that make them more reactive as is indicative by their increased ring strain.[21] This is also evident for the **15**→**18** conversion by an increased exothermicity ($\Delta E_{\mathbf{11}\rightarrow\mathbf{14}}$ = 21.7; $\Delta E_{\mathbf{15}\rightarrow\mathbf{18}}$ = 25.6 kcal·mol^{-1}). Additionally, the analogous rearrangement for the fluoro-substituted 2-phospha-4-silabicyclo[1.1.0]butane **19** confirms this trend ($\Delta E_{\mathbf{19}\rightarrow\mathbf{20}}$ = 28.1 kcal·mol^{-1}, Figure 7). Furthermore, the associated transition state of this novel pathway is stabilized by the electron donating N-heterocyclic substituent on silicon ($\Delta E^{\ddagger}_{\mathbf{11}\rightarrow\mathbf{14}}$ = 39.0, $\Delta E^{\ddagger}_{\mathbf{15}\rightarrow\mathbf{18}}$ = 27.7, $\Delta E^{\ddagger}_{\mathbf{19}\rightarrow\mathbf{20}}$ = 35.0 kcal·mol^{-1}).

8.5 Conclusion

Hetero substitution changes the stability of the valence isomers of bicyclo[1.1.0]butane (**1**). 2-Phospha-4-silabicyclo[1.1.0]butane (**11**) is the least stable isomer and 1,2-dihydro-1,2-phosphasilete (**14**) the most stable one at the QCISDT/6–311+G**//QCISD/6–31G* level of theory.[22] Two reaction pathways for the thermal isomerization of 2-phospha-4-silabicyclo[1.1.0]butane (**11**) have been found: (a) a three step process starting with a barrier of 38.8 kcal·mol^{-1} for the

concerted, asynchronous conrotatory ring opening of **11** to *s-trans*-1-phospha-4-sila-1,3-butadiene (**12**), followed by a conformational change to the *gauche* isomer **13** and a subsequent conrotatory electrocyclic ring closure to **14**, and (b) a direct transformation of **11** into **14** via a [σ2s+σ2a] process with a barrier of 39.0 kcal·mol^{-1} which becomes favorable when electron donating substituents are present on silicon. This latter path is unprecedented for the analogous isomerization of bicyclo[1.1.0]butane.

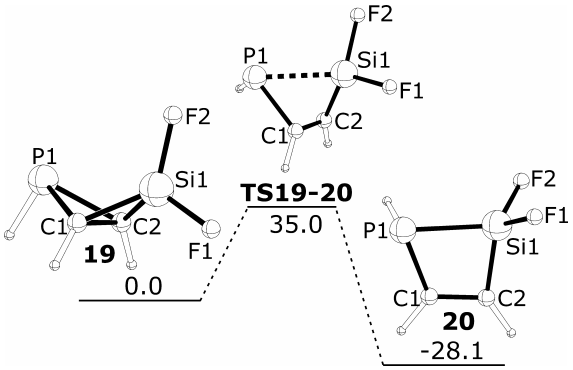


Figure 7. Relative QCISDT/6–311+G**//QCISD/6–31G* energies (ZPE corrected, in kcal·mol^{-1}) for the direct rearrangement of **19** into **20**. Selected bond lengths [Å] and torsion angles [°] of **19** (C_s): P1-C1 1.852, Si1-C1 1.797, Si1-F1 1.600, C1-C2 1.631, C1-P1-C2 52.2, C1-Si1-C2 54.0, P1-C1-C2-Si1 122.0; **TS19-20**: P1-C1 1.834, P1-Si1 2.383, Si1-C2 1.758, Si1-F1 1.613, Si1-F2 1.610, C1-C2 1.457, P1-C1-C2-Si1 77.5; **20**: P1-C1 1.879, P1-Si1 2.252, Si1-C2 1.841, Si1-F1 1.607, C1-C2 1.357.

8.6 Computational Section

All calculations were performed using the GAUSSIAN 98[23] suite of programs. Geometries were optimized using the standard 6–31G* basis set at the (U)MP2 and (U)QCISD[24] level of theory, while single point calculations have been preformed at the (U)QCISDT/6–311+G** level using the (U)QCISD/6–31G* geometries. First and second order energy derivatives were computed to confirm that minima or transition structures had been located at the (U)MP2/6–31G* level. Intrinsic reaction coordinate driving calculations (IRC) were performed at the (U)MP2/6–31G* level to establish connections between transition structures and minima. The total energies calculated at the (U)MP2, (U)QCISD and (U)QCISDT levels have been corrected for the (U)MP2/6–31G* level zero-point energies scaled by a factor of 0.967.[25]

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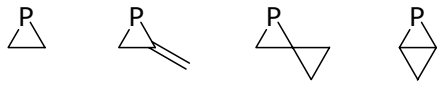
Samenvatting

Het onderzoek beschreven in dit proefschrift, getiteld "Highly Strained Organophosphorus Compounds" of te wel "Hooggespannen Organofosforverbindingen", is gericht op het verkrijgen van een beter inzicht in de eigenschappen en toepassingen van kleine, gespannen fosforhoudende ringsystemen. Deze verbindingen zijn van fundamenteel belang vanwege hun bijzondere elektronische en chemische eigenschappen. Daarnaast zijn deze deeltjes, door hun hoge ringspanning, vaak thermisch labiel en geven via verscheidene transformaties toegang tot een palet van nieuwe organofosforverbindingen, die op geen enkele andere wijze eenvoudig te synthetiseren zijn. Als gevolg hiervan zijn toepassingen van deze interessante ringstructuren in zicht gekomen, zoals het gebruik als bouwsteen (fosfine ligand) in nieuwe katalysatoren of als uitgangsmateriaal voor de bereiding van nieuwe fosforhoudende materialen.

Het uitgangspunt bij dit onderzoek is de primaire ringstructuur **1**, genaamd fosfiraan, die een ringspanning bezit van 21 kcal·mol^{-1}. Wij hebben ons tot doel gesteld om ringstructuren te synthetiseren die nog meer ringspanning bevatten dan **1**, middels het introduceren van een exocyclische dubbele binding (methyleenfosfiraan **2**) of door het fuseren van meerdere drieringen via een hoekpunt, zoals fosfa[2]triangulaan **3**, of via een zijde, zoals fosfabicyclo[1.1.0]butaan **4**.



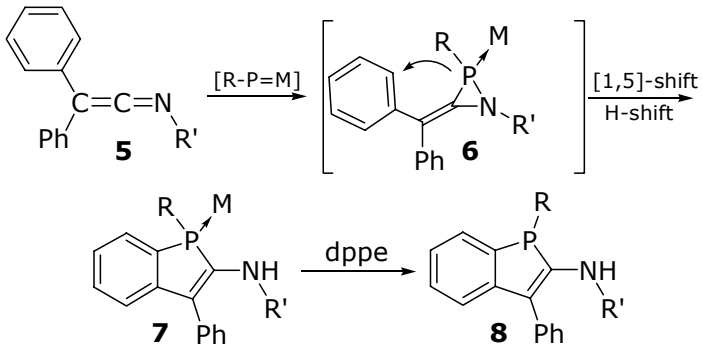
1 **2** **3** **4**

Om deze doelstellingen te verwezelijken zijn reactieve intermediairen gebruikt bij de experimentele onderzoekingen, zoals de laag-valente carbenen, fosfinidenen en silylenen. De gedane ontdekkingen en bevindingen zijn vervolgens onderbouwd met nauwkeurige theoretische berekeningen, om zodoende de bewandelde reactiepaden en -mechanismen te kunnen analyseren en ophelderen.

In het inleidende hoofdstuk van dit proefschrift wordt een uiteenzetting gegeven van alle bekende fosforhoudende drieringen, waarbij voornamelijk de toepassingen van

deze interessante klasse van verbindingen belicht worden. De nadruk ligt in dit hoofdstuk op het gebruik van deze deeltjes als ligand in homogene katalyse of als bouwsteen in de vervaardiging van nieuwe, gefunctionaliseerde polymeren.

In hoofdstuk 2 wordt de reactiviteit van electrofiele fosfinideencomplexen besproken in de aanwezigheid van keteenimines **5**, wat resulteert in de synthese van de unieke 2-aminofosfaindeen complexen **7** (Schema 1). Theoretische berekeningen (UB3LYP/6–31G*), en het gebruik van het ijzer-gecomplexeerde fosfinideen *i*Pr_2N-P=Fe$(CO)_4$, hebben aangetoond dat methyleenazafosfiraan **6** het tussenproduct is in de vorming van complex **7**. De opmerkelijk selectieve omzetting van **6** naar **7**, waarbij de aromaticiteit in een phenyl-substituent tijdelijk wordt opgeheven, vindt plaats door middel van een [1,5]-sigmatrope omlegging gevolgd door een protonverhuizing van koolstof naar stikstof. Deze unieke transformatie wordt mogelijk gemaakt door de aanwezigheid van de exocyclische C=C binding en het stikstofatoom als protonacceptor in **6**. Beide facetten zijn essentieel, anders kan de vorming van **7** niet plaatsvinden.

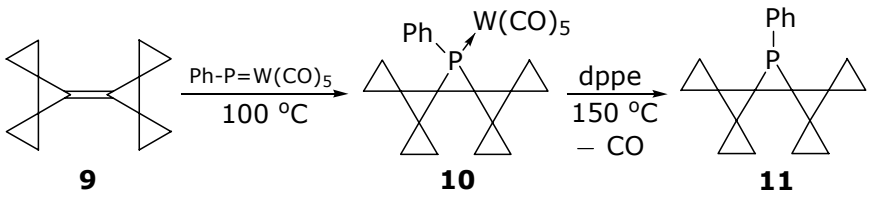


Schema 1. Synthese van 2-aminofosfaindenen **7** and **8**.

De 2-aminofosfaindenen **7** kunnen ook gedecomplexeerd worden, waardoor een effectieve 2-staps synthese ontstaat (totaal opbrengst = 76% voor R,R'=Ph) van de 2-aminofosfaindeen liganden **8** uitgaande van de makkelijk toegankelijke keteenimines **5**.

Hoofdstuk 3 en 4 beschrijven het resultaat van een samenwerkingsverband met de onderzoeksgroep van prof.dr. A. de Meijere van de Georg-August-Universität

Göttingen in Duitsland. In hoofdstuk 3 wordt de synthese van het eerste hetero[7]triangulaan **10** beschreven, wat gevormd wordt uit singlet fosfinideen Ph-P=W(CO)$_5$ en tweede-generatie bicyclopropylideen **9**. Triangulaan **10**, bestaande uit 7 spiro-verknoopte drieringen, is ondanks zijn totale ringspanning van 224 kcal·mol^{-1} thermisch stabiel, en kan zelfs gedecomplexeerd worden in kokend xyleen, door middel van een ligand uitwisseling, waarbij het stabiele en esthetische vrije fosfine **11** in hoge opbrengst verkregen wordt (84%, Schema 2).

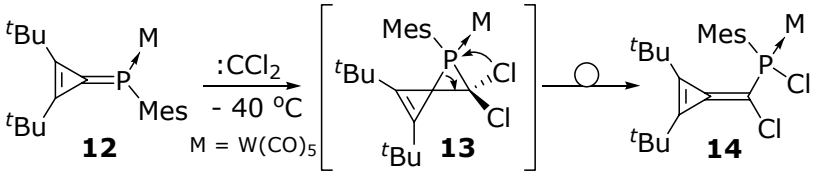


Schema 2. Synthese van fosfa[7]triangulanen **10** and **11**.

De uitzonderlijke thermische stabiliteit tot wel 150 °C van beide triangulanen is opvallend, aangezien de meeste fosfiranen stuk gaan bij een veel lagere temperatuur (≤ 110 °C) door het uitstoten van het fosfinideen Ph-P=W(CO)$_5$ of door het breken van een van de P–C bindingen. De stabiliteit van **10** en **11** wordt toegeschreven aan de unieke π-donor en π*-acceptor capaciteiten van het electronrijke olefine **9**, gevoegd bij het vrijkomen van olefinespanning in **9** (23 kcal·mol^{-1}) tijdens de vorming van de PCC ring.

In hoofstuk 4 wordt het onderzoek verder uitgebreid met de synthese van 10 nieuwe lineaire en vertakte mono- en bisfosfa[*n*]triangulanen, die allen uitzonderlijk stabiel zijn. In tegenstelling tot het vorige hoofdstuk wordt bij de syntheses nu het reactieve fosfinideen gegenereerd met behulp van een katalytische hoeveelheid koperchloride, in plaats van thermische eliminatie uit de 7-fosfanorbornadiëen precursor. Dit heeft tot gevolg dat het reactieve deeltje geen vrij fosfinideen is maar een koperhoudend [PhP(Cl)W(CO)$_5$]-Cu-O complex (O = olefine of oplosmiddel). Zichtbare veranderingen in de reactiviteit treden alleen op als de reactieve dubbele binding van het substraat minder goed toegankelijk is, waardoor bijproducten ontstaan die zonder gebruik van een katalysator niet worden waargenomen.

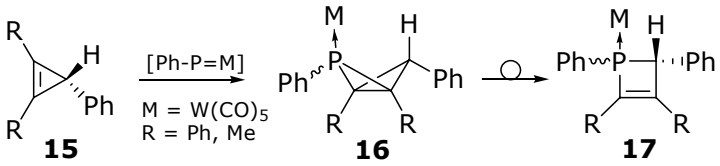
Hoofdstuk 5 behandelt de verknoping van een fosfiraan met cyclopropenen in plaats van de cyclopropanen uit hoofdstuk 3 en 4. Dit leidt nu tot instabiele verbindingen. Dichloorcarbeen-additie aan de exocyclische C=P binding van fosfatriafulveen **12** geeft, zelfs bij lage temperaturen (–40 °C), direct het nieuwe fosfor-gesubstitueerde triafulveen **14** met fosfaspiropenteen **13** als vermoedelijk tussenproduct, dat helaas niet kan worden waargenomen (Schema 3).



Schema 3. Fosfaspiropenteen **13** als tussenproduct.

Voor soortgelijke fosfiraancomplexen, weliswaar zonder cyclopropeen substituent, is een identieke transformatie gerapporteerd die pas bij 110 °C optreedt. Dit geeft aan dat cyclopropenen de PCC ring van een fosfiraan destabiliseren, dit in scherp contrast tot cyclopropanen die een stabiliserend effect hebben.

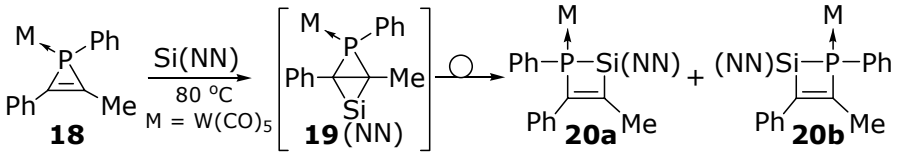
Hoofdstuk 6 bespreekt het samensmelten van 2 cyclopropanen via een C–C binding wat leidt tot de vorming van de hooggespannen bicyclo[1.1.0]butanen (68 kcal·mol^{-1} ringspanning) welke, sinds hun ontdekking in 1959, nog volop in de belangstelling staan. De fosforhoudende analoga zijn echter nog steeds maar beperkt bekend. Wij hebben ons tot doel gesteld om de eigenschappen van de onbekende 2-fosfabicyclo[1.1.0]butanen **16** te onderzoeken, die gesynthetiseerd kunnen worden door het fosfinideen Ph-P=W(CO)$_5$ te laten reageren met de cyclopropenen **15** (Schema 4).



Schema 4. Het eerste 2-fosfabicyclo[1.1.0]butaan **16**.

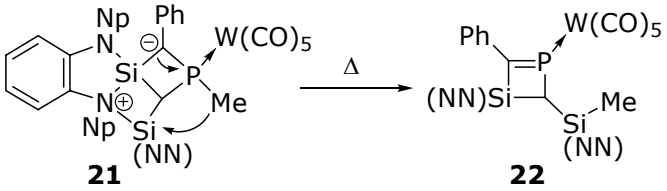
De eerste 2-fosfabicyclo[1.1.0]butanen **16**, gesynthetiseerd en gekarakteriseerd met behulp van een kristalstructuuropheldering, zijn thermisch niet stabiel en transformeren via een valentie isomerisatie naar de stabielere fosfacyclobutenen **17**. Deze omlegging wordt beinvloed door de substituenten op het bruggenhoofd van de bicyclische ringstructuur (**16**-Ph 50 °C; **16**-Me 130 °C) wat volledig in overeenstemming is met de transformaties van de analoge koolstofwaterstoffen.

Hoofdstuk 7 beschrijft het resultaat van een samenwerkingsverband met dr. B. Gehrhus van de University of Sussex in Brighton, Engeland. In dit hoofstuk worden onze onderzoekingen naar het onbekende 2-fosfa-4-silabicyclo[1.1.0]butaan **19** behandeld, gebruikmakend van een andere aanpak dan in hoofdstuk 6. Reactie van het thermisch stabiele silyleen Si[$(NCH_2{}^tBu)_2C_6H_4$-1,2] [≡Si(NN)] met 1*H*-phosphireen **18** resulteert in de vorming van 2-fosfa-4-silabicyclo[1.1.0]butaan **19** als tussenproduct, dat niet kan worden waargenomen doordat dit direct een valentie isomerisatie ondergaat naar de stabielere fosfasilacyclobutenen **20** (Schema 5).



Schema 5. Isomerisatie van bicyclo[1.1.0]butaan **19**.

Het verloop van deze reactie kan worden beinvloed door de substituenten. Zonder de aanwezigheid van de methylgroep op het bruggenhoofd in **19** kunnen twee equivalenten Si(NN) reageren met 1*H*-phosphireen **18** en wordt het unieke zwitterion **21** gevormd als kinetisch product, dat door verwarmen fosfasileet **22** geeft als thermodynamisch product (Schema 6).



Schema 6. Isomerisatie van zwitterion **21**.

In het laatste hoofdstuk van dit proefschrift wordt, gebruikmakend van zeer nauwkeurige ab initio berekeningen (QCISDT/6–311+G**//QCISD/6–31G*), de experimentele bevindingen van hoofdstuk 7 theoretisch onderbouwd. Hieruit blijkt dat 2-fosfa-4-silabicyclo[1.1.0]butaan **19** direct kan isomeriseren via een toegestane Woodward–Hoffmann [σ2s+σ2a] omlegging naar de thermodynamisch stabielere P,Si-cyclobutenen **20**. Dit reactiepad is nog niet eerder experimenteel vastgesteld en heeft de voorkeur boven een asynchrone ringopening die leidt naar de corresponderende P,Si-butadienen, welke het gunstigste is voor de analoge koolwaterstoffen.

Op grond van de studies aan hooggespannen organofosforverbindingen beschreven in dit proefschrift, kan geconcludeerd worden dat deze unieke ringstructuren uitermate interessant zijn vanuit een synthetisch oogpunt maar ook functioneel zijn als bouwsteen in de vervaardiging van velerlei producten. Vaak geeft de organofosforchemie vergelijkbare resultaten met de analoge koolwaterstofchemie, maar dikwijls worden ook significante verschillen gevonden waarbij de aanwezigheid van fosfor unieke structuren en/of reactiepaden mogelijk maakt die niet bestaan of toegankelijk zijn voor de corresponderende koolwaterstoffen.

Dankwoord

De proeven en het geschrift zijn voltooid – laat de wijn rijkelijk vloeien! Na 174 bladzijden van wetenschappelijke arbeid, die u als lezer uitvoerig gelezen heeft - toch?, is dit de plaats voor een persoonlijke noot. Uiteraard ben ik velen dankbaar voor het totstandkomen van dit boekwerk. Alleen had ik deze klus zeker niet kunnen klaren.

Allereerst wil ik graag mijn promotor, *prof.dr. Koop Lammertsma*, bedanken voor de mogelijkheid om mijzelf als promovendus te ontwikkelen en voor de grote vrijheid in het onderzoek die ik heb genoten. Uw messcherpe analyses en heldere kijk op mijn werk hebben mij altijd bij de les gehouden en hebben het schrijven van de manuscripten zeker bevorderd.

Ook mijn copromotoren *dr. Marius Schakel* en *dr. Andreas W. Ehlers* ben ik veel dank verschuldigd voor de dagelijkse begeleiding. Beste Marius, jouw zorgvuldige correcties van voornamelijk het experimentele gedeelte in mijn manuscripten zijn werkelijk opzienbarend. Beste Andreas, uiteindelijk heb je me toch aan het rekenen gekregen wat geresulteerd heeft in een solide theoretische onderbouwing van mijn experimentele werk. Helaas geen succesvolle synthese van het fosfatetrahedraan, ons ultieme doelmolekuul en een geweldig idee van jouw promotor prof.dr. G. Frenking, maar Niels en ik zijn een eind gevorderd.

I would like to thank *Prof. Dr. G. Bertrand*, *Prof. Dr. H. Grützmacher*, *Prof. Dr. F. Bickelhaupt*, *Prof. Dr. C. J. Elsevier*, and *Prof. Dr. L. W. Jenneskens* for being the referees of this thesis.

dr. Frans J. J. de Kanter: Hartelijk dank voor jouw snelle hulp en expertise op NMR-gebied waardoor al mijn nieuwe verbindingen zorgvuldig zijn gekarakteriseerd.

Dr. Barbara Gehrhus: I am very pleased that we continued our succesful collaboration that started, together with Prof. Dr. M. F. Lappert, in 1999 in Brighton. Many thanks for your generous gifts of the carbene C[$(NCH_2{}^tBu)_2C_6H_4$-1,2] and your precious silylene Si[$(NCH_2{}^tBu)_2C_6H_4$-1,2].

prof.dr. Anthony L. Spek, dr. Martin Lutz, en dr. Allison M. Mills: Jullie kristal-structuurbepalingen zijn van topkwaliteit! en zijn van onschatbare waarde geweest bij de identificatie van vele verbindingen tijdens mijn promotieonderzoek. Vooral de structuuropheldering van bijprodukt 7 (H3) en zwitterion 6b (H7) is vakwerk.

Prof. Dr. Armin de Meijere und Dr. Sergei I. Kozhushkov: Ich möchte mich bei Ihnen ganz herzlich für die von Ihnen erhaltenen hochgespannten olefinischen polycyclischen Kleinringverbindungen bedanken. Diese Verbindungen werden in meiner Promotionsarbeit in den Kapiteln 3 und 4 thematisiert und die Synthesen von unseren neuen Phospha[*n*]triangulanen sind bereits publiziert worden.

Prof. Dr. Ian Manners, Dr. Eric Rivard, Lawrence A. Vanderark, and Timothy J. Clark: Our collaboration was initiated at the International Symposium on Inorganic Ring Systems in Burlington, Vermont (USA) and resulted in a novel approach to organophosphorus polymers. Your efforts are greatly appreciated!

Tom Nijbacker: Jouw vele tips en trucks hebben het begin van mijn promotietijd zeker vereenvoudigd. Tevens veel dank voor jouw hulp bij de synthese van Stephan's zirkoniumfosfinideen $Cp_2Zr(PMe_3)$=PMes*. Helaas door de vele lopende projecten heb ik onze reactiviteitsstudies met Barbara's silyleen niet kunnen voltooien. Maar het bestuderen van deze metathesereactie verdient zeker een tweede kans.

*dr. Herman Zappe*y en *dr. Marek Smoluch*: Bedankt voor het meten van talrijke exacte massa's die vooral tijdens de eindfase van mijn promotieonderzoek, toen de druk het hoogst was, ongekend snel verkregen werden.

*dr. Mark Vlaa*r en *Danielle Vugts*: Als beginnende promovendus heb ik het erg fijn gevonden om het succesvolle keteenimine-project voort te zetten. Weliswaar heb ik er tijdens mijn gehele promotietijd aan gewerkt, maar nu is het toch afgerond.

De studenten die een belangrijke rol gespeeld hebben tijdens het onderzoek, *Winita Merhai* (hoofdvak), *Tanja Eichelsheim* (HLO), *Willem-Jan van Zeist, Tijmen de Boer*, *Daniele Gibney* (eindproject) en *Niels Elders* (master), wil ik bedanken voor hun inzet en de mooie resultaten die behaald zijn. Willem-Jan, jouw eerste dichloor-carbeenadditie was meteen raak en heeft geleid tot een mooie publicatie. Niels, jij hebt mijn meest uitdagende project vanaf het begin grondig aangepakt. Ondanks dat veel van onze ideeën strandden heb je aan het eind toch succes geboekt.

Mark Borst: Na onze studietijd én onze promotietijd samen met veel plezier beleefd te hebben scheiden nu toch onze wegen, maar eerst nog samen feest!

Ook wil ik alle andere collega's bedanken voor de geweldige werksfeer en gezelligheid, ook buiten werktijd, met name Mark Vlaar, Jan, Rosa, Fedor, André, Sander, Marcel, Erik, Halil, Helen, Rob, Bas de Jong, Peter, Judith, Romano, Mieke, Danielle, Robin, Bas Groenendaal, Edith, en Alessia.

Tenslotte wil ik hier nog een aantal mensen noemen die buiten de chemie een belangrijke rol gespeeld hebben.

Willem Dijkstra: Neef, hartelijk dank voor een sterk staaltje digitale fotografie. Je hebt het stukje pyromorfiet uitstekend op de plaat weten vast te leggen.

Corniel Nobel: Jouw opzetje voor de lay-out van dit proefschrift is veel waard geweest, maar ik ben je het meest dankbaar voor de schitterende omslag!!

Nu rest alleen nog de openbare verdediging van mijn proefschrift. Bij voorbaat wil ik *Patrick Duin* en *Danny Kwint* danken voor het feit dat zij mij tijdens de promotie, als paranimf, terzijde willen staan.

Wouter en Willie: Hartelijk dank voor alle gezelligheid in huize Jansen en voor jullie belangstelling in mijn bezigheden op de VU. Spoedig zal ook jullie dochter zo'n bestseller afleveren.

Pa en Ma: Door jullie nimmer aflatende steun en vertrouwen heb ik mijn eigen weg kunnen vinden. Zonder jullie had ik dit hoogtepunt nooit kunnen bereiken. Waarschijnlijk zullen jullie aan de inhoud van dit proefschrift weinig plezier beleven, maar ik hoop dat de promotieplechtigheid dat zeker goedmaakt.

Helen: Als laatste wil ik uiteraard jou bedanken. Ik heb enorm genoten van de keren dat we samen mijn manuscripten grondig hebben geanalyseerd en van de juiste, naar onze mening, Engelse bewoording hebben voorzien. Maar uiteraard reikt onze chemie verder dan de wetenschap. Ik ben zielsgelukkig dat we elkaar hebben gevonden en ik dank je voor al jouw steun, liefde en vertrouwen. Jij bent mijn alles!

Zürich, september 2005.

Chris

Curriculum Vitae

De schrijver van dit proefschrift, Jacob Christiaan Slootweg, werd geboren op 7 maart 1978 te Haarlem. Na het behalen van het Atheneum diploma in juni 1996 aan de Scholengemeenschap Wiringherlant te Wieringerwerf, verhuisde Chris naar Amsterdam alwaar hij Scheikunde studeerde aan de Vrije Universiteit. In het kader van deze studie deed hij zijn eerste onderzoeksstage bij de sectie Organische en Anorganische Chemie (prof.dr. K. Lammertsma), met als onderwerp organofosforchemie. Aansluitend verbleef Chris vijf maanden in Brighton, Engeland waar hij onderzoek deed in de organosiliciumchemie aan de University of Sussex (prof.dr. M. F. Lappert, dr. B. Gehrhus). Zijn laatste onderzoeksstage deed Chris aan de Universiteit van Amsterdam (prof.dr. P. W. N. M. van Leeuwen) met als specialisatie homogene katalyse. De studie werd afgesloten met een scriptie over zwak coördinerende anionen. Na het afleggen van zijn doctoraal examen in april 2001, startte hij in mei van datzelfde jaar zijn promotieonderzoek in de organofosforchemie onder leiding van prof.dr. K. Lammertsma, een terugkeer bij de sectie Organische en Anorganische Chemie. Tijdens deze periode van vier jaar werden de behaalde resultaten gepresenteerd op nationale en internationale symposia in binnen- en buitenland, zoals het International Symposium on Inorganic Ring Systems (Burlington, Vermont, USA) en het International Conference on Phosphorus Chemistry (Birmingham, Engeland). Deze werkbezoeken hebben geleid tot velerlei contacten resulterend in verscheidene internationale samenwerkingsverbanden. Het promotieonderzoek heeft geleid tot het thans gereedgekomen proefschrift. Vanaf 1 juli 2005 is de schrijver werkzaam als postdoc in de onderzoeksgroep van prof.dr. P. Chen aan de ETH in Zürich, Zwitserland, waarvoor hij een TALENT-stipendium heeft ontvangen van de Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO).

Curriculum Vitae

The author of this thesis, Jacob Christiaan Slootweg, was born on March 7th 1978 in Haarlem, the Netherlands. In June 1996, at the age of 18, Chris graduated from high school at the Scholengemeenschap Wiringherlant in Wieringerwerf. After the summer of 1996, Chris went to Amsterdam to study chemistry at the Vrije Universiteit where he specialized in organic chemistry. His studies were concluded with three different research projects and a thesis. The first project focused on organophosphorus chemistry (Prof. Dr. K. Lammertsma), this was followed by a five month project in organosilicon chemistry at the University of Sussex in Brighton, England (Prof. Dr. M. F. Lappert, Dr. B. Gehrhus). Finally, a research project was undertaken in homogeneous catalysis at the University of Amsterdam (Prof. Dr. P. W. N. M. van Leeuwen). His master's thesis concentrated on weakly coordinating anions and led to a master's degree in April 2001. In May 2001, Chris returned to the group of Prof. Dr. K. Lammertsma at the Vrije Universiteit to start a 4-year Ph. D. in organophosphorus chemistry, of which this thesis is the end result. As a Ph. D. student, Chris presented his work at several inspiring international conferences, like the International Symposium on Inorganic Ring Systems (Burlington, Vermont, USA) and the International Conference on Phosphorus Chemistry (Birmingham, England) and consequently, quite a few collaborations were initiated and resulted in a number of scientific papers. Starting from July 1st 2005, Chris is working as a postdoctoral fellow in the group of Prof. Dr. P. Chen at the ETH in Zürich, Switzerland, for which he received a TALENT stipend of the Netherlands Organization for Scientific Research (NWO).

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B. Gehrhus, P. B. Hitchcock, M. F. Lappert, J. C. Slootweg, "The Diverse Reactions of the Silylene Si[$(NCH_2tBu)_2C_6H_4$-1,2] with Li[$Si(SiMe_3)_3$]$(thf)_3$ and K[$N(SiMe_3)_2$]", *Chem. Commun*. **2000**, 1427–1428.

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A work such as this is actually never complete.

One must declare it to be complete when one has done all that is possible given the time and the circumstances.

Johann Wolfgang von Goethe, "Italian Journey" (1787)